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by

V. Percec

Submitted

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Handbook of Liquid Crystal Research

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Peter J. Collings and J. S. Patel

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From Molecular to Macromolecular Liquid Crystals

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CONTENTS

8.1 HISTORICAL REVIEW

8.2 INTRODUCTION TO LIQUID CRYSTALS

8.2.1 Molecular Liquid Crystals and Definitions

8.2.2 Macromolecular Liquid Crystals

8.3 ISOMORPHISM OF LIQUID CRYSTALS

8.4 ON THE "RIGIDITY" OF "ROD-LIKE" MESOGENS

8.4.1 Rigid Rod-Like Mesogens

8.4.2 Semirigid Rod-Like Mesogens

8.4.3 Flexible Rod-Like Mesogens

8.5 MOLECULAR DESIGN OF PHASE TRANSITIONS THROUGH STRUCTURAL VARIATIONS. SOME THERMODYNAMIC CONSIDERATIONS

8.5.1 Equilibrium States

8.5.2 Metastable States

8.5.3 Influence of Molecular Weight on Phase Transition Temperatures

8.5.3.1 Both Monomeric Structural Unit and Polymer Display an Enantiotropic Mesophase

8.5.3.2 The Monomeric Structural Unit Displays a Virtual or a Monotropic Mesophase; The Polymer Displays a Monotropic or an Enantiotropic Mesophase

8.5.3.3 The Monomeric Structural Unit Displays a Virtual Mesophase; The Polymer Displays a Virtual Mesophase

8.5.3.4 Rigid Rod-Like Polymers

8.6 MAIN CHAIN LIQUID CRYSTALLINE POLYMERS

8.6.1 Soluble and Fusible Main Chain Liquid Crystalline Polymers

8.6.1.1 Poly(p-phenylene) and its Derivatives

8.6.1.2 Metal Containing Poly(ynes)

8.6.1.3 Spinal Columnar Liquid Crystalline Polymers

8.6.1.4 Aromatic Polyamides and Polyesters

8.6.1.5 Rod-Like Soluble Polyimides

8.6.1.6 Thermotropic Poly(1,4-arylenevinylene)s

8.6.1.7 Other Conjugated Polymers

8.6.1.8 Polyurethanes

8.6.1.9 Polycarbonates

8.6.1.10 Poly(ester anhydride)s

8.6.1.11 Poly(ester imide)s

8.6.1.12 Polyhydrocarbons

8.6.1.13 Polyethers

8.6.1.14 Liquid Crystalline Fluorocarbon-Hydrocarbon

Copolymers

8.6.2 Persistence Lengths of Soluble Polyesters and Polyamides

8.7 CHEMICAL HETEROGENEITY IN MAIN CHAIN LIQUID CRYSTALLINE COPOLYMERS

8.8 FLEXIBLE AND SEMIFLEXIBLE LIQUID CRYSTALLINE POLYETHERS

8.9 HYPERBRANCHED AND DENDRIMERIC LIQUID CRYSTALLINE POLYMERS

8.10 CYCLIC MAIN CHAIN LIQUID CRYSTALLINE OLIGO- AND POLYETHERS

8.11 SIDE CHAIN LIQUID CRYSTALLINE POLYMERS

8.11.1 General Considerations

8.11.2 Molecular Engineering of Liquid Crystalline Polymers by Living Polymerization

8.11.2.1 General Considerations

8.11.2.2 Influence of Molecular Weight on the Phase Transitions of Poly{ ω -[(4-cyano-4'-biphenyl)oxy]alkyl vinyl ether}s

8.11.2.3 Molecular Engineering of Liquid Crystalline Phases by Living Cationic Copolymerization

8.11.2.4 Side Chain Liquid Crystalline Polymers Exhibiting a Reentrant Nematic Mesophase

8.11.2.5 Influence of Tacticity on Phase Transitions

8.11.2.6 Cyclic Polysiloxanes Containing Mesogenic Side Groups

8.11.2.7 Side Chain Liquid Crystalline Polyacetylenes

8.12 IONIC LIQUID CRYSTALLINE POLYMERS

8.12.1 Main Chain Ionene Liquid Crystal Polymers

8.12.2 Side Chain Ionic Liquid Crystal Polymers

8.12.3 Liquid Crystalline Polyelectrolyte Complexes

8.13 LIQUID CRYSTALLINITY INDUCED VIA INTER- AND INTRACHAIN ELECTRON-DONOR-ACCEPTOR (EDA) INTERACTIONS

8.14 LIQUID CRYSTALLINE POLYMERS CONTAINING CROWN ETHERS AND POLYPODANTS

8.15 ELECTRON DONOR-ACCEPTOR (EDA) COMPLEXES OF LIQUID
CRYSTALLINE POLYMERS CONTAINING DISCOTIC MESOGENS

8.16 MOLECULAR RECOGNITION DIRECTED SELF-ASSEMBLY OF
SUPRAMOLECULAR LIQUID CRYSTALLINE POLYMERS. H-
BONDING AND OTHER INTERACTIONS

ACKNOWLEDGMENTS

REFERENCES

8.1 HISTORICAL REVIEW

Onsager (Onsager, 1949) and Flory (Flory, 1956) predicted that rigid rod-like macromolecules should display liquid crystallinity. The first main chain thermotropic liquid crystalline polymer was reported in open literature in 1975 (Roviello and Sirigu, 1975). This publication was independent from the flexible spacer concept advanced by deGennes (deGennes, 1975) in the same year. Patents on thermotropic main chain liquid crystalline polymers were however published starting with 1973 (Jackson, Jr. and Kuhfuss, 1976; Kuhfuss and Jackson, Jr., 1973; 1974). Some interesting publications dealing with the driving force behind the development of main chain thermotropic crystalline polymers and various historical variants of these developments are available (Ballauff, 1989; Blumstein and Blumstein, 1988; Economy, 1989; 1990 A; Finkelmann, 1987; Gordon and Platé, 1984 A; 1984 B; Jackson, Jr., 1989).

Although the field of thermotropic side chain liquid crystalline polymers is older than that of thermotropic main chain liquid crystalline polymers, systematic investigations in this field started only after Ringsdorf et al. introduced the spacer concept (Finkelmann et al., 1978 A, 1978 B). Monographs and review articles on side chain and main chain liquid crystalline polymers are available (Blumstein, 1978 A, 1978 B; 1983; 1985; Chapoy, 1985; Chiellini and Lenz, 1989; Ciferri et al., 1982; Ciferri, 1991; Collins, 1990; Donald and Windle, 1991; Gordon and Platé, 1984 A, 1984 B; Gray, 1987; Griffin and Johnson, 1984; Luckhurst and Gray, 1979; McArdle, 1989; Noël and Navard, 1991; Percec and Pugh, 1989 A; Percec and Tomazos, 1992 Q; Percec et al, 1992 S; Platé and Shibaev, 1987; Platé, 1993; Saeva, 1979; Weiss and Ober, 1990; Zentel, 1989 B).

The goal of this chapter is to discuss the dependence between various molecular parameters including structure, molecular weight, architecture, etc. and phase behavior. An attempt will be made to follow this trend on passing from a molecular to a macromolecular liquid crystal. The main goal is to provide the reader with the presently available tools which can be used to tailor-make liquid crystalline polymers. A brief and general introduction to low molar mass and polymeric liquid crystals which is required for this purpose will also be made.

8.2.1 Molecular Liquid Crystals and Definitions

Mesogens or mesogenic groups are compounds which under suitable conditions give rise to liquid crystalline phases, i.e., mesophases. They can be classified in non-amphiphilic (i.e. most frequently hydrogenated or hydrophobic compounds exhibiting a rod-like or disc-like shape) and amphiphilic (i.e. compounds that contain within the same molecule hydrophobic and hydrophilic groups which have the ability to dissolve in organic solvents and water respectively). Thermotropic mesophases are induced by a change in temperature, while lyotropic mesophases are induced by a solvent, which can be either water or organic. Some mesogens can generate amphotropic mesophases, i.e. the liquid crystalline phase can be induced either by a change in temperature, by a solvent, or by both (Ringsdorf et al., 1988). Other highly immiscible groups like perfluorinated and paraffinic, available within the structure of the same molecule also give rise to amphotropic mesophases (Hopken et al., 1988; Mahler et al., 1985; Viney et al., 1989 A, 1989 B).

Depending on their thermodynamic stability with respect to the crystalline phase, thermotropic mesophases can be virtual (unstable with respect to the crystalline phase), monotropic (metastable with respect to the crystalline phase), or enantiotropic (stable with respect to the crystalline phase) (Keller et al., 1990; Percec and Keller, 1990 E). Virtual mesophases exist only below the melting and crystallization temperature and therefore can not be observed. Monotropic mesophases can be observed only during cooling due to the fact that the crystallization process is kinetically controlled and therefore is supercooled, while the liquid crystalline phase is thermodynamically controlled and is not supercooled. Enantiotropic mesophases can be observed both on heating and cooling. A detailed discussion on the conversion of a mesophase from virtual into monotropic and into enantiotropic will be presented later.

Traditionally, thermotropic mesophases exhibited by rod-like or calamitic mesogens can be classified in uniaxial, biaxial, and chiral nematic (cholesteric), and a number of different smectic phases which form either an untilted layer (smectic A, s_A etc.) or a tilted layer (smectic C, s_C etc.) structure. Characteristic for the nematic phase is a parallel orientation of the molecules along an axis that corresponds to the long axis of the mesogen. While uniaxial nematic phases (biaxial nematic (Galerne, 1967) phases will not be discussed here) exhibit a one-dimensional order, smectic phases can exhibit a two-dimensional (s_A , s_C exhibiting unstructured layer structures) or a three-dimensional (s_B , s_G , s_E , s_H exhibiting structured layer structures) order (Gray and Goodby, 1984). Therefore, s_B , s_G , s_E and s_H liquid crystalline phases are in fact crystalline. Disc-like mesogens exhibit various columnar or discotic mesophases (Chandrasekhar, 1982; 1992;

Chandrasekhar and Ranghnath, 1990) i.e., racemic and chiral nematic (n_D), columnar hexagonal or discotic (Φ_h or D), etc. Plastic crystals are a class of mesophases in which spherical shaped molecules, though orientationally completely disordered, reside (with minor fluctuations) at the points of a spatial lattice, i.e., there is positional order but orientational disorder (e.g., methane, carbon tetrachloride, carbon tetrafluoride, camphor, cyclohexanol, etc.).

Upon increasing their concentration, amphiphilic mesogens generate isotropic, and then micellar solutions. At higher concentrations rod-like micells generate hexagonal mesophases while spherical micells generate cubic mesophases. Alternatively an isotropic solution of an amphiphilic molecule can assemble directly into a lamellar liquid crystalline phase (DeGiorgio et al, 1985; Kelker and Hatz, 1980; Lehman, 1922; Pershan, 1979; Rinne, 1933; Seddon and Templer, 1991; Skoulios and Guillon, 1988; Winsor, 1968). Cubic mesophases do not exhibit a texture since they are optically isotropic. The discotic hexagonal mesophase obtained from discotic mesogens, the hexagonal mesophase of amphiphilic molecules and the columnar hexagonal mesophase displayed by conformationally disordered polymer chains (Ungar, 1993) are from symmetry point of view identical.

8.2.2 Macromolecular Liquid Crystals

Based on the place of the polymer where the mesogen is inserted, i.e. within the main chain, as side groups, or both within the main chain and as side groups, liquid crystalline polymers can be classified into main chain, side chain and combined (Figure 1). Polymers with more complex architectures are also possible

(Demus, 1988; 1989; Percec and Pugh, 1989 A; Ringsdorf et al, 1988). The mesogen used in the construction of the liquid crystalline polymer can be rod-like, disc-like, amphiphilic, etc. (Demus, 1988; 1989; Finkelmann et al, 1984; Hopken et al, 1988; Jahns and Finkelmann, 1987; Luhman and Finkelmann, 1986; 1987; Mahler et al, 1985; Percec and Pugh, 1989 A; Ringsdorf et al, 1988; Ringsdorf and Wustefeld, 1990; Viney et al, 1989 A; 1989 B). In addition to linear polymer structures, cyclic (Percec and Hahn, 1989 C; Richards et al, 1990), hyperbranched (Kim, 1992 A; 1992 B; Percec et al, 1992 I; 1994 G; Percec and Kawasumi, 1992 L), dendrimeric (Percec, 1995 B; Percec and Chu, 1995 C) and crosslinked (Gleim and Finkelmann, 1989; Zentel, 1989 A) architectures have also been synthesized. Therefore, liquid crystalline polymers display thermotropic and lyotropic mesophases which are similar to those exhibited by thermotropic and lyotropic low molar mass liquid crystals. In addition, rigid-rod like main chain non-amphiphilic polymers like poly(phenyleneterephthalamide) (Kevlar®) (Bair et al, 1977; Kwolek et al, 1977; Morgan, 1977; Panar and Beste, 1977), poly(*p*-phenylene-2,6-benzobisthiazole) and poly(*p*-phenylene-2,6-benzobisoxazole) (Papkov, 1984) also exhibit lyotropic nematic mesophases.

The backbone of side chain liquid crystalline polymers adopts a random-coil conformation only in ideal solution and in isotropic melt. In the nematic phase the conformation of the polymer backbone is slightly distorted, while in a smectic phase is highly distorted and can even be confined to the smectic layer (Davidson et al, 1991; Davidson and Levelut, 1992; Noël, 1989, 1988; Noël and Navard, 1991; Noirez et al, 1988; 1995; Pepy et al, 1988; Percec and Pugh, 1989 A; Percec et al, 1990 C; Percec and Tomazos, 1990 I).

8.3 ISOMORPHISM OF LIQUID CRYSTALS

The miscibility of low molar mass liquid crystals and of polymers is important both for the identification of various liquid crystalline phases and for the preparation of mixtures with well defined phase transitions. Arnold, Sackmann, and Demus have developed the miscibility rules (Arnold and Sackmann, 1960 A, 1960 B; Demus et al, 1983; Krigbaum, 1985; Sackmann and Demus, 1973) which can be summarized as follows: if two liquid crystalline phases are miscible, they are isomorphic, and therefore belong to the same type of mesophase. However, the reverse is not true. The situation is more complicated for mixtures of liquid crystalline polymers with low molar mass liquid crystals and for mixtures of liquid crystalline polymers. Many times similar phases of liquid crystalline polymers and low molar mass liquid crystals are not miscible (Achard et al, 1988; Benthack-Thoms and Finkelmann, 1985; Casagrande et al, 1982; Krigbaum, 1985; Ringsdorf et al, 1982, Sigaud et al, 1987; Tinh et al, 1990). The same is the case for similar phases of two different liquid crystalline polymers (Percec and Tsuda, 1991 Q). A general discussion on this topic and a comparison of isomorphism of crystalline and liquid crystalline polymers and of isomorphism of structural units in copolymers is available (Percec and Tsuda, 1991 Q). When two compounds are isomorphic within a certain mesophase, both their thermal transition temperatures and corresponding thermodynamic parameters exhibit continuous dependencies versus composition. The same is the case for a copolymer. When its structural units are isomorphic within a certain phase, the corresponding transition temperatures and thermodynamic parameters exhibit continuous dependencies on composition. This means that both the components of mixtures and the structural units of copolymers

behave like an ideal solution. Therefore, by knowing the temperature transitions and thermodynamic parameters of the parent compounds we can apply the equations of Schroeder and Van Laar (eq. 1) and predict the phase diagram of the mixture or of the copolymer (Achard et al, 1988; Schroeder, 1893; Van Hecke, 1979; Van Laar, 1908).

$$F_1 = \left\{ 1 - \frac{\Delta H_1^{\circ} T_2 (T - T_1)}{\Delta H_2^{\circ} T_1 (T - T_2)} \right\}^{-1} \quad \text{Eq. 1}$$

where F_1 is the molar fraction of component 1, T_1 and ΔH_1 are the transition temperature and the enthalpy change of pure component 1, T_2 and ΔH_2 have the same meaning for component 2, while T is the transition temperature corresponding to molar fraction F_1 . T should be lower than T_2 and higher than T_1 . Thus, a phase diagram that exhibits a higher or smaller temperature transition than the maximum or minimum T_2 or T_1 respectively, violates the T criteria discussed above and must therefore, be discussed by the introduction of nonideality of solution of structural units of the copolymer. The negative, positive or linear dependence of T versus F_1 is determined by the parameter A from Eq. 1.

$$A = \frac{\Delta H_1^{\circ} T_2}{\Delta H_2^{\circ} T_1} \quad \text{Eq. 2}$$

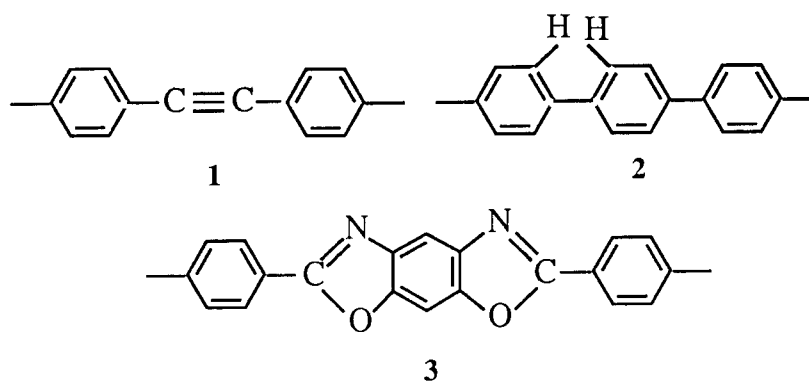
8.4 ON THE "RIGIDITY" OF "ROD-LIKE" MESOGENS

The conventional procedure used to design low molar mass liquid crystals (Demus, 1989, 1988; Gray, 1962; 1974; 1979; 1982), main chain (Ballauff, 1989; Blumstein and Blumstein, 1988; Economy, 1989; 1990 A; Finkelmann, 1987; Gordon and Platé, 1984 A; Jackson, Jr., and Kuhfuss 1976; Jackson, Jr.; 1989;

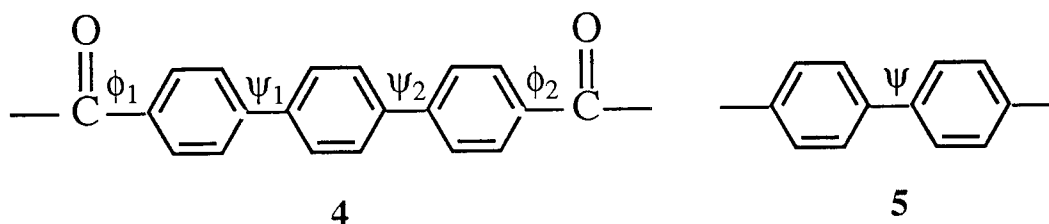
Kuhfuss and Jackson, Jr., 1974) and side-chain (Finkelmann et al, 1978 A; 1978 B; 1984; Percec and Pugh, 1989 A) liquid crystalline polymers is based on the use of *rigid rod-like* mesogenic units. Recently, the concept of *flexible rod-like* mesogens or *rod-like* mesogens based on *conformational isomerism* was introduced and used in the synthesis of both side chain (Hsu and Percec, 1987; 1989; Percec and Pugh, 1989 A) and main chain (Bilibin et al, 1989; Memeger, 1991; Percec and Yourd, 1988 A; 1989 D, 1989 I; Percec and Tsuda, 1990 B; 1990 D; Ungar et al, 1990) liquid crystalline polymers. Low molar mass liquid crystals based on *flexible rod-like mesogens* were discussed elsewhere (Hsu and Percec, 1987; 1989; Percec and Pugh, 1989 A; Percec and Yourd, 1988 A; 1989 D, 1989 I; Percec and Tsuda, 1990 B; 1990 D; Ungar et al, 1990). Depending on their conformational or configurational rigidity we have suggested the classification of *rod-like* mesogenic groups as *rigid rod-like*, *semirigid* or *semiflexible rod-like* and *flexible rod-like* mesogens (Percec and Zuber, 1991 O).

8.4.1 Rigid Rod-Like Mesogens

Rigid rod-like mesogens such as diphenylacetylene **1**, oligo-*p*-phenylene **2**, and benzoxazole **3** and other similar derivatives are based on linearly substituted aromatic or heterocyclic rings. They exhibit free rotation about certain C-C bonds as in the case of **1-3**, but this rotation does not perturb their elongated or extended shape, and therefore these molecules retain their *rigid rod-like* character. Consequently, in *rigid rod-like mesogenic units*, rigid refers to the rigidity of the linear shape.

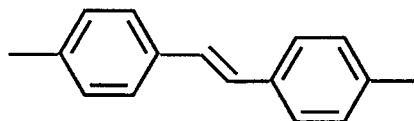


In oligo-*p*-phenylene (2) the steric interaction of the ortho hydrogens impede this internal rotation and the conjugation effect reinforces the rigidity due to the double bond character of the C-C bond between the phenylene rings. An energy barrier of 5 kcal/mol for the internal rotation of the outer rings of 4 was obtained experimentally (Tékély et al, 1983), while conformational calculations provided for this rotation a value of about 4.8 kcal/mol (Meurisse et al, 1984). The minimum energy is at $\phi_1=\phi_2=0$ or $\phi_1=0, \phi_2=180^\circ$.



In the case of 5, the energy barrier is of 1.9 kcal/mole and the minimum energy is at $\phi=40^\circ$. This value is in agreement with the experimental data obtained in vapor state (i.e. $\phi=42^\circ$) (Meurisse et al, 1984). If the aromatic rings are connected via a double bond as in the case of stilbene 6, the trans isomer is energetically more favorable. It can be isomerized into the cis form, but the activation energy for this transformation is very high and, therefore, makes this

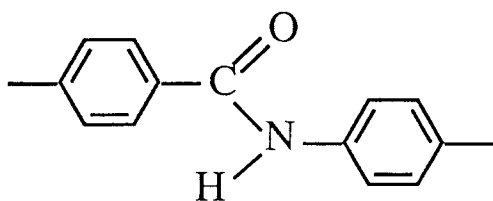
molecule rigid. An activation energy of 42.8 kcal/mol was reported for the thermal uncatalyzed isomerization of stilbene (Kalinowski and Kessler, 1973).



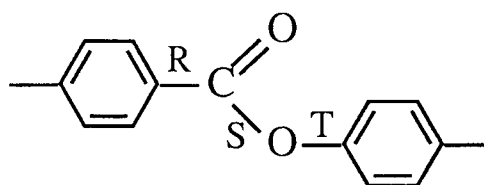
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8.4.2 Semirigid Rod-Like Mesogens

Semirigid rod-like mesogens such as amides **7** and esters **8** have both conformational and configurational character. Due to electronic reasons, the rotation about the C-O or C-N bond of **7** and **8** is retarded and or even prohibited. In esters like **8**, there is rotation about the R, S and T bonds.



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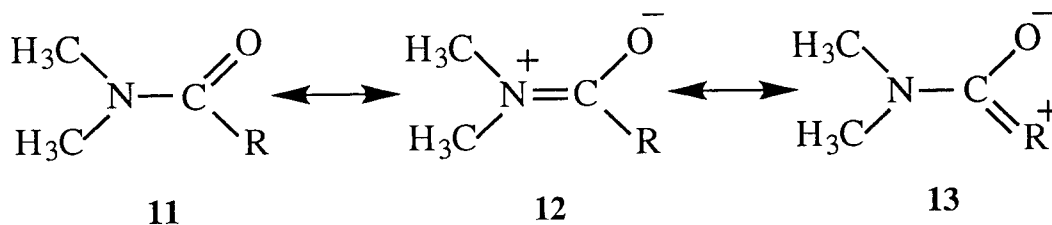
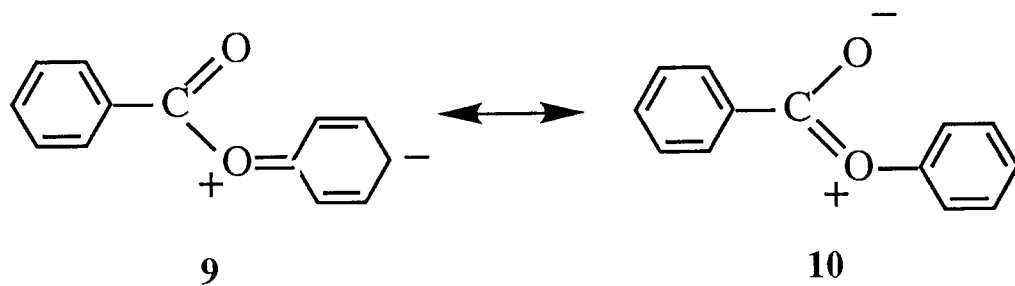


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The most significant rotation is about the S-bond, since it determines the kinked (*cis*) or extended (*trans*) conformation of the molecule. Theoretical calculations (Coulter and Windle, 1989) suggest the *trans* conformation to be the most stable. The *trans*-form of esters and acids has a better $O_n-C\sigma^*$ "hyperconjugation" which decreases their free energy (Coulter and Windle, 1989). The steric effect in the *cis* form makes it less stable than the *trans* form. The potential energy of the *cis* form is higher than that of the *trans* form with 7.9 kcal/mol. In the energy profile there is a hump at 90° which is due to the $O_p-C\pi^*$ overlap which creates a double bond character on the O-C bond. This barrier is smaller for aromatic esters than for

aliphatic esters because the delocalization of p-electrons of the oxygen on the aromatic ring attached to the oxygen gives the structure **9** which competes with the contributor **10**. This conclusion is supported by the difference between the C-O bond length of aliphatic and aromatic esters. The C-O bond length is 1.33 Å in alkyl benzoate and 1.36 Å in aryl benzoate (Coulter and Windle, 1989). This value is the closest to the typical ether C-O bond length of 1.42-1.43 Å. This double bond character creates a configurational character for the *cis* and *trans* conformers of esters and amides and subsequently, these compounds behave close to the class of rigid mesogens. Therefore, they should be classified as *semirigid* or *semiflexible rod-like mesogens*.

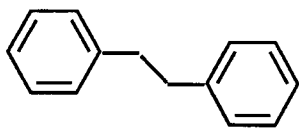
The structure and conformational behavior of amides **7** is very close to that of esters **8**. The different resonance structures **11**, **12** and **13** of a typical amide molecule (Kessler, 1970) are similar to those of esters. Due to its double bond character, the contribution of **12** hinders the rotation about the C-N bond.



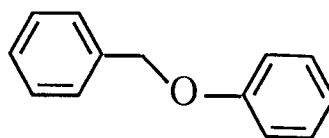
A rotational energy barrier of 21 kcal/mol which corresponds to about 40% double bond character for the C-N bond of amides was predicted (Kessler, 1970). This double bond character decreases due to the participation of (13), especially when R = aryl and was demonstrated by NMR studies performed on $(\text{CH}_3)_2\text{N}-\text{C}(\text{O})-\text{R}$. When R is CH_3 - the rotational energy barrier is 18.9 kcal/mol (Mannschreck, 1965) and decreases to 14.4 kcal/mol (Mannschreck et al, 1967) for R= phenyl. A rotational energy barrier of about 20 kcal/mol for the rotation about the C-N bond of phenyl benzamide was experimentally obtained (Tashiro et al, 1977).

8.4.3 Flexible Rod-Like Mesogens

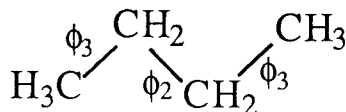
1,2-Disubstituted ethane **14** and methyleneoxy or benzylethers **15** belong to the class of flexible rod-like mesogenic units. Let us briefly recapitulate the conformational behavior of n-butane **16**. Out of its conformational isomers, the most stable are the *gauche* **17** and **18** and the *anti* **19**. Depending on the experimental technique used, an energy difference of 0.6 (Bartell and Kohl, 1963), 0.68 (Woller and Garbisch, Jr., 1972), 0.77 (Szasz et al, 1948), or 0.966 ± 0.054 (Verma et al, 1974) kcal/mol between the *gauche* and the *anti* conformers of n-butane was reported.



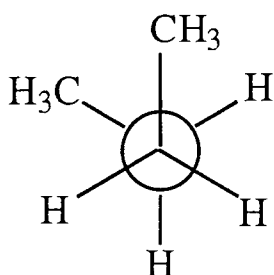
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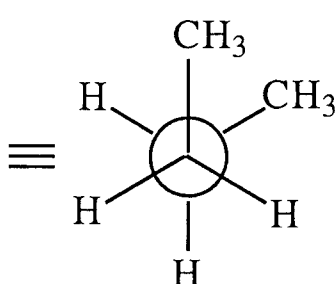
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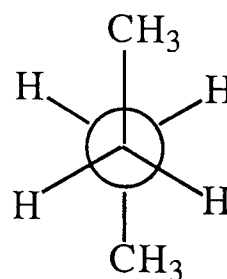
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Theoretical calculations (Darsey and Rao, 1981) led to a rotational energy barrier at $\phi_2=60^\circ$ (when CH_3 - group is eclipsed with a hydrogen atom) of 3.7 kcal/mol and to a potential energy difference of 1.19 kcal/mol. A rotational energy barrier of 2.8 kcal/mol and a potential energy difference of 0.53 kcal/mol were calculated (Abe et al, 1966). Consequently, the theoretical and experimental results of n-butane agree.

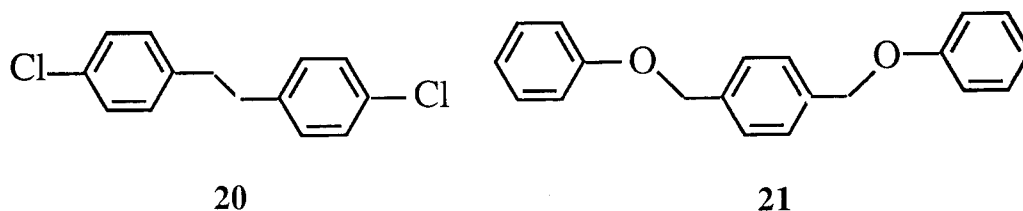
An X-ray study (Brown, 1954) of diphenyl ethane and IR and Raman investigations (Chiu et al, 1972) performed on 1,2-diphenyl ethane and 1,2-di(*p*-chlorophenyl)ethane (**20**) demonstrated that all three molecules exist in solid state as *anti* conformers. An optical anisotropy study (Unanue and Bothorel, 1965) performed by diffusion Rayleigh depolarization on solutions of 1,2-diphenylethane

in CCl₄ and cyclohexane, shows that the anti conformer is preferred also in solution. Solution and Nujol mulls (Chiu et al, 1972) investigations of para substituted 1,2-diphenylethane derivatives showed at 25°C a ratio of *anti* to *gauche* of 84:16. However, in case of 1,2-diphenylethane (**14**) the concentration of *gauche* conformer is too low to be detected by IR spectroscopy. A ¹³C-NMR spectroscopy study (Reuvers et al, 1969) of 1,2-di(2,6-dimethylphenyl)ethane performed in CCl₄ solution showed a dynamic equilibrium of 7/3 between the *anti* and *gauche* conformers.

The results of theoretical calculations performed on 1,2-diphenylethane are contradictory. It has been shown that the *gauche* conformer of **14** is more stable than the anti one with 0.57 kcal/mol (Ivanov et al, 1976). Jacobus (Jacobus, 1976) reported that the *gauche* conformer is more stable with 1.15 kcal/mol than the *anti*. A theoretical study (Petteron and Liljefors, 1987) provided data which are in agreement with the experimental results, suggesting that the *anti* form is more stable than the *gauche* form. The energy difference between these conformers is of 0.95 kcal/mol and increases to 1.59 kcal/mol when point charge and electrostatic interactions are also considered. Jonsson et al. (Jonsson et al., 1989; 1990 A; 1990 B) calculated the conformational energy barrier of α,α' -diphenyl-*p*-xylene (**21**), which is a model compound for the polymers based on benzyl ether mesogenic units. The potential energy barrier to move one of the outer rings to the position where it becomes linear is 3.87 kcal/mol.

A theoretical calculation on main chain polyethers containing flexible benzyl ether mesogens showed that 50% of the mesogenic group should be in their *gauche* conformation at the temperature they are in the liquid crystalline phase (Petracone

and Pirozzi, 1991). The mesogenic groups of the polymer are, however, at this temperature in their *anti* conformation. The formation of the liquid crystalline phase which favors a linear chain conformation provides the driving force for the change of the dynamic equilibrium between the *anti* and *gauche* conformers.



From this discussion it is clear that in the crystalline state only the *anti* conformer exists. However, in solution both the *anti* and the *gauche* conformers exist in a dynamic equilibrium. To our knowledge, the rotational energy barrier of 1,2-diphenylethane is not available. Ivanov et al. (Ivanov et al., 1976) calculated the potential energy at different values of torsional angle (Ph-C-C-Ph) i.e., when they are in the *anti*, *gauche*, and *eclipse* forms. In the *eclipse* form, the two rings are in the closest geometry (the steric and other nonbonded interactions are maximum). Depending on the method used, the calculated energy of the *eclipse* form is 3.61, 3.49 and 1.95 kcal/mol. This conformer has the maximum potential energy suggesting that the conformational energy barrier should be lower than the above mentioned values because during the *gauche* to *anti* or *anti* to *gauche* conformational change the benzene rings eclipse with the ethylenic hydrogen atoms, and this steric interaction is less than for two benzene rings.

In conclusion, based on the difference between the rotational energy barrier of different configurational isomers or conformers of rod-like mesogens we suggested (Percec and Zuber, 1991 O) their classification into three categories:

rigid, semirigid or semiflexible, and flexible. Rigid rod-like groups are rigid units whose shape is rigid like for example (1), (2), and (3), and configurational isomeric units which require a high rotational energy barrier or activation energy, like for example stilbene ($\Delta E_a=42.8$ kcal/mol). *Semirigid or semiflexible rod-like* mesogens are conformationally flexible, but due to some electronic reasons they behave like configurational isomers of medium rotational energy barrier. Classic examples are aromatic amides and esters ($\Delta E_a=14.4$ kcal/mol and 7.1 kcal/mol respectively). The rotational energy barrier of these molecules is less than half that of rigid molecules but is much higher than that of flexible molecules. *Flexible rod-like* mesogens are conformationally flexible groups whose rotational energy barrier is within the same range of values with that of butane ($\Delta E_a=2.8-3.7$ kcal/mol). Classic examples are phenylbenzylether ($\Delta E_a=3.87$ kcal/mol) and 1,2-diphenylethane ($\Delta E_a=3.61$ kcal/mol) based molecules.

8.5 MOLECULAR DESIGN OF PHASE TRANSITIONS THROUGH STRUCTURAL VARIATIONS. SOME THERMODYNAMIC CONSIDERATIONS

8.5.1 Equilibrium States

For the discussion which follows (Keller et al, 1990; Percec and Keller, 1990 E) it will be sufficient to consider the basic thermodynamic relationship:

$$dG = VdP - SdT \quad \text{Eq. 3}$$

where G is the free energy, S the entropy, V the volume, P the pressure and T the temperature. We will consider first the melting of a true crystal at constant pressure

($dP=0$). The free energies of both crystal (G_k) and isotropic liquid (G_i) decrease with increasing temperature where the decrease in G_i is the steeper, due to $S_i > S_l > S_k$ (Figure 2, Eq. 3). Where G_i crosses G_k the crystal melts (i.e., at $T_{k-i} = T_m$). In this case, the free energy of any hypothetical liquid crystalline phase, G_{lc} , cannot fall below both G_k and G_i . While G_{lc} decreases faster with T than G_k it will only cross G_k at a point which is above G_i , i.e. where the isotropic liquid is already the stablest phase. Thus the mesophase is virtual and remains unrealizable as a stable phase.

In order to create a stable mesophase a section of the G_{lc} versus T curve will need to be brought beneath both G_k and G_i . This can be achieved either a) by raising G_i (Figure 3), or b) by raising G_k (Figure 4), or by a combination of both a) and b). As seen in Figures 3 and 4 the mesophase will be "*uncovered*" in a temperature range bounded by T_{k-lc} and $T_{lc-i} = T_i$ corresponding to temperatures of crystal melting and isotropization respectively. (The lowering of G_{lc} would have the same effect; but changes in G_{lc} are expected to be small compared to those in G_i and G_k and will be disregarded in what follows.) In general, raising of G_i (Figure 3) arises from the lowering of the melt entropy (i.e., by increasing the rigidity of the molecule via a permanent structural change or via a temporary change such as shear or any other kind of orientation, constraint or pressure), while raising of G_k (Figure 4) from the reduction in the perfection of the crystal (i.e., by copolymerization or other kind of chemical and/or physical modification) T_m decreases and therefore G_k increases. Note that in case of Figure 3 the crystal melting point, T_m , is raised, while in that of Figure 4 it is lowered.

We can generalize further by considering the influence of change in pressure, i.e. the VdP term in Equation 3. Usually the specific volume is larger for the liquid than for the crystal with the mesophase expected to lie in between; hence $(dG_k/dP)_T < (dG_{lc}/dP)_T < (dG_i/dP)_T$. In principle it could therefore happen that at some P G_{lc} falls below G_k and thus a mesophase may become "*uncovered*". It has been found that in most experimental systems (Bassett, 1982) the effect of increased hydrostatic pressure is to promote the mesophase ("barophyllic" behavior). However, there is no fundamental reason that would make this a general rule. This is clearly illustrated by the example of the sequence of alkanes \rightarrow polyethylene (as it is described in detail elsewhere (Keller et al, 1990) where "barophobic" behavior of short n-alkanes changes continuously with increasing chain length toward the "barophyllic" behavior of polyethylene (Ungar, 1986).

8.5.2 Metastable States

Figures 2-4 refer to states of thermodynamic equilibrium. However, systems may not respond immediately when passing from one stable regime to another within the phase diagram, hence the metastable phases can often arise. The most commonly encountered metastability is that arising on crystallization. As familiar, crystallization only sets in at certain supercooling. In polymers in particular, crystallization temperature $T_{i \rightarrow k}$ can be appreciably below the equilibrium melting point $T_{k \rightarrow i} = T_m$. On the other hand, the formation of a mesophase generally requires less supercooling. Now, if the temperature from the isotropic liquid to a normally unstable mesophase is located between $T_{k \rightarrow i}$ and

$T_{i \rightarrow k}$, such a "virtual" mesophase may materialize on cooling. As the temperature is lowered still further, crystallization will occur. At this state two extreme situations may be envisaged (Figures 5 and 6). On crystallization the free energy either drops from G'_k to G_k , i.e. the value for the perfect (Figure 5, where the dotted line indicates a possible pathway), or else there is no continuous change in G , i.e. a highly imperfect crystal is formed with its free energy remaining at G'_k (Figure 6). The realistic path would be somewhere in between these two extremes, i.e. some decrease in G is expected, which may not quite reach the level of G_k .

We shall first consider the extreme situations of Figures 5 and 6. When the perfect crystal of Figure 5 is reheated, it melts directly into the isotropic liquid at $T_{k \rightarrow i}$; thus such a system displays the mesophase only on cooling, and is called "*monotropic*". On the other hand, the imperfect crystal of Figure 6 first changes back into the mesophase at $T_{k'-lc}$ and then into the isotropic liquid at T_{lc-i} on reheating. Subsequently the mesophase occurs both on cooling and heating and is called "*enantiotropic*". The latter case clearly illustrates that an enantiotropic mesophase does not necessarily mean stability of the mesophase, as sometimes implied, although a stable mesophase, naturally, must be enantiotropic. As mentioned before, real systems are in between those described by Figures 5 and 6. Some decrease below G'_k will occur upon crystallization, the magnitude of the drop depending, among others, on crystallization kinetics. Accordingly, neglecting possible perfectioning on subsequent heating, mono- and enantiotropic behavior are distinguished by the magnitude of the drop in G on crystallization; if G stays above a critical value (G_k^c) the system is enantiotropic, if it falls below it is monotropic, the definition of G_k^c being apparent from Figure 5. It is easily seen how crystal

perfectioning on annealing can lead to a "conversion" of an enantiotropic into a monotropic mesophase, an effect frequently observed in both polymeric and low molar mass liquid crystals.

It is worth noting further that, under certain conditions, polymers will also display superheating effects, in which case the mesophase may only appear on heating; this can be regarded as "monotropic" behavior in the reversed sense. An example of this in connection with polyethylene was discussed previously (Keller et al, 1990) and an example with a side chain liquid crystalline polymer was reported recently (Percec et al, 1991 S).

Finally a further kinetic factor, the glass transition (T_g), will be considered. On cooling the system becomes immobilized at T_g , hence phase transformations will be arrested or all together prevented. The inverse will apply when a previously immobilized system is heated above T_g when the system will again be able to follow its course towards the equilibrium state. In practice, this will lead to inaccessibility of certain portions of the phase diagram, or conversely, lead to the freezing in of the liquid or of the liquid crystalline state enabling their attainments at temperatures where by thermodynamic criteria they would be unobtainable otherwise (isotropic or liquid crystalline glass respectively). Even if T_g is not a thermodynamic quantity the indication of its location in the phase diagram can therefore serve as a useful purpose.

General examples from literature following the patterns of the thermodynamic schemes described above are provided elsewhere (Keller et al, 1990).

8.5.3 Influence of Molecular Weight on Phase Transition Temperatures

We will now discuss the relationship between phase transition temperatures and polymer molecular weight for three different situations (Keller et al, 1990; Percec and Keller, 1990 E). Upon increasing the molecular weight from monomer to polymer, the entropy of the liquid phase (S_i) decreases. The decrease of the entropies of mesomorphic and crystalline phases is lower than that of the isotropic phase. For simplicity, the decrease of the entropy of the crystalline phase will be neglected. The decrease in S_i and S_{lc} tends asymptotically to zero with increasing molecular weight (M). M_0 from Figures 7 to 9 refers to the molecular weight of the polymer structural unit. M_1 to M_∞ from the same figures are arbitrary molecular weights of the corresponding polymer. It follows that G_i and G_{lc} increase with the increase of the polymer molecular weight again asymptotically; above a certain molecular weight, we may consider both parameters as remaining almost constant.

8.5.3.1 Both Monomeric Structural Unit and Polymer Display an Enantiotropic Mesophase

The first situation considered refers to the case in which the monomeric structural unit displays an enantiotropic mesophase. Upon increasing its molecular weight to dimer, trimer, etc., S_i decreases and, therefore, G_i increases. Beyond a certain molecular weight, G_i remains for all practical considerations constant. Figure 7 transforms the free energy (G) versus transition temperature (T) dependence, into a transition temperature (T) versus molecular weight (M) dependence. The T versus M plot in Figure 7 demonstrates that both melting (T_{k-lc})

and isotropization (T_{lc-i}) temperatures increase with molecular weight up to a certain range of M values beyond which T_{k-lc} and T_{lc-i} remain approximately constant with the T_i line lying above the line for T_m for all molecular weights. However, the slope of the increase of T_{lc-i} is steeper than that of T_{k-lc} . The difference between these two slopes determines the relative thermodynamic stabilities of the mesomorphic versus that of the crystalline phases at different polymer molecular weights.

For this particular case, the higher slope of the T_{lc-i} - M versus that of the T_{k-lc} - M dependence leads to a widening of the temperature range between the two curves with increasing molecular weights of the polymer. This widening of the liquid crystal temperature regime with molecular weight agrees with experimental data reported for the case of both main chain (Blumstein et al, 1982; Feijoo et al, 1988; Godovsky et al, 1985; Percec et al, 1987 B) and side chain (Kostromin et al, 1982; Percec and Pugh, 1989 A; Percec and Hahn, 1989 F; Percec and Lee, 1991 A; 1991 C; 1991 G; 1991 H; 1991 I; 1991 J; 1991 N; Percec and Tomazos, 1992 A; Percec et al, 1989 J; 1991 B; 1991 E; 1991 F; 1991 P; 1991 T; 1992 R) liquid crystalline polymers. This effect has been repeatedly labeled as the "*polymer effect*", especially in the case of side chain liquid crystal polymers (Percec and Pugh, 1989 A).

8.5.3.2 The Monomeric Structural Unit Displays a Virtual or a Monotropic Mesophase; The Polymer Displays a Monotropic or an Enantiotropic Mesophase

The steeper slope of the $T_{lc-k(i)}$ - M dependence versus that of the $T_{k-i(lc)}$ - M dependence has even more important implications on the molecular weight-phase transition temperature dependence for the situation when the monomer structural unit displays only a monotropic or a virtual mesophase (Figure 8).

As seen the two lines T_i versus M and T_m versus M intersect. This arises from the fact that $T_i < T_m$ for low molecular weights with a steeper slope for T_i . Specifically (for the illustration in Figure 8) the T_i (i.e. T_{lc-k}) values are below the corresponding T_m (i.e. T_{k-i}) values for M_0 to M_4 , hence in the range M_0 to M_4 , i.e. the monomer together with its low oligomers up to 4, display only a virtual mesophase. Beyond M_4 the mesophase becomes stable, hence the system enantiotropic. In addition to the thermodynamic criterion, kinetics also influence the phase transitions. A certain amount of supercooling of the isotropic-mesomorphic and especially much more so of the mesomorphic-crystalline transitions is possible which can lead to monotropic behavior for molecular weights slightly below and at the intersection point (i.e. at M_4). In view of the fact that T_i and T_m are expected to be continuous functions of molecular weight, the intersection point can be arbitrarily closely approached (from below), hence realization of a metastable liquid crystal phase and subsequent monotropic behavior is to be expected for appropriate molecular weights in cases to which Figure 8 pertains. This effect has been observed experimentally both in the case of main chain (Feijoo et al, 1988; Majnusz et al, 1983; Percec and Nava, 1987 A; Zhou et al, 1986) and side chain (Percec and Tomazos, 1992 A; Stevens et al, 1984) liquid crystalline polymers and was labeled "*transformation of a monotropic mesophase*".

into an enantiotropic mesophase by increasing the molecular weight of the polymer". A series of quantitative experiments on this line will be described later.

8.5.3.3 The Monomeric Structural Unit Displays a Virtual Mesophase; The Polymer Displays a Virtual Mesophase

The third situation is illustrated in Figure 9 and also refers to a different case in which the monomeric unit displays only a virtual mesophase. Here as before, the slope of the T_i (i.e. T_{lc-k})- M dependence is higher than that of the T_m (i.e. T_{k-i})- M dependence, the latter lies above the former throughout hence the two curves do not intercept each other. Therefore, the resulting polymer displays also a virtual mesophase. This thermodynamic situation was recently applied to the synthesis of liquid crystal polyethers containing both flexible mesogens and flexible spacers and exhibiting virtual liquid crystalline phases (Percec and Yourd, 1988 A; 1989 D; 1989 I; Percec and Tsuda, 1990 B; 1990 D; Ungar et al, 1990) and will be detailed in a subsequent chapter.

8.5.3.4 Rigid Rod-Like Polymers

The discussion from Cases 1 to 3 refers to semiflexible or semirigid and flexible polymer systems which exhibit first order transition temperatures (i.e. melting, isotropization) which are molecular weight dependent only up to a certain degree of polymerization. In these systems the melting temperature is determined by the length of the chain fold. Rigid rod-like polymers such as poly(p-phenylene)s, poly(p-phenylenebenzobisthiazole) (PBT), poly(p-phenylenebenzobisoxazole) (PBO) etc. should exhibit a linear dependence of their

melting transition over their entire range of molecular weights. Consequently, the dependencies of their first order transitions on molecular weight should follow the pattern from Figure 10. Table 1 summarizes the dependence of the first order transition temperatures of poly(p-phenylene)s $H-(C_6H_4)_n-H$ as a function of their degree of polymerization and their axial ratio ($x=L/d$) (Flory and Ronca, 1979, Irvine et al, 1984, Sigaud, 1992) (Figure 11a). As predicted by theory (Flory, 1956; Flory and Ronca, 1979), when the axial ratio ($x=L/d$) of rod-like molecules reaches a value of about 6.2 the compound should exhibit an enantiotropic mesophase. This is indeed the case. For n of 6 or 7 poly(p-phenylene)s exhibit an enantiotropic nematic mesophase (as predicted by Figure 10). At lower n values the nematic mesophase is virtual. However, for oligomers with n larger than 7 the nematic mesophase cannot be observed since the decomposition temperature first overlaps the melting transition and then becomes lower than the melting temperature. Other rigid rod-like polymers like PBT and PBO and even semirigid systems like fully aromatic and unsubstituted polyamids and polyesters decompose before melting.

While in rigid rod-like polymers the axial ratio $x=L/d$ (Figure 11a) defines the chain dimension which is responsible for the generation of an enantiotropic mesophase, in the case of semi-rigid and flexible polymers the ratio l/d (Figure 11b) (where l is now a renormalized length i.e., the Kuhn's segment) defines it. In this second case the higher l , the higher the stiffness of the chain (Sigaud, 1992).

In conclusion, the steeper slope of the isotropization temperature-molecular weight dependence versus that of the melting temperature-molecular weight dependence should have the following effects on transforming a monomer into a

polymer. When the monomer structural unit displays an enantiotropic mesophase, the resulting polymer will display a broader enantiotropic mesophase. When the monomeric unit displays a monotropic mesophase, the resulting polymer will, most probably, display an enantiotropic mesophase. When the monomeric unit displays a virtual mesophase, the resulting polymer may display either an enantiotropic, monotropic or virtual mesophase. For the case of side chain (Percec et al, 1989 J; Stevens et al, 1984) and main chain (Blumstein et al, 1982; Percec and Nava, 1987 A; Zhou et al, 1986) liquid crystalline polymers containing flexible spacers and displaying a single mesophase, the nature of the mesophase displayed by the polymer is most frequently identical to that of its monomeric unit. Primarily the molecular weight-phase transition dependences are determined by the relationship between the free energies of the crystalline, liquid crystalline and isotropic phases of the monomeric structural unit yet influenced by the molecular weight of the main chain backbone through its effect on the melt entropy as in Case 1 above. Combinations of more than one mesomorphic phases of different thermodynamic stabilities in a monomeric structural unit will follow the same molecular weight dependence trend as those described for the monomers displaying a single mesophase (Percec and Lee, 1991 A; 1991 H; Percec et al, 1991 B; 1991 E; 1991 F; 1991 P; 1992 R). However, there are few examples where the nature of the mesophase displayed by the main chain and side chain liquid crystalline polymers is molecular weight dependent. Both in the case of the main chain (Blumstein and Blumstein, 1988; Kumar et al, 1988;) and side chain (Percec et al, 1991 E; Percec and Lee, 1991 A; 1991 H; 1991 G; 1994 F; Percec and Tomazos, 1992 A; Percec and Oda, 1994 H; 1994 I; 1995 A) liquid crystalline polymers it has been

demonstrated that this change in the mesophase represents a continuous dependence of molecular weight. In the case of rigid rod-like polymers both melting and isotropization temperatures reach higher values than the decomposition temperature within the range of low molecular weights.

8.6 MAIN CHAIN LIQUID CRYSTALLINE POLYMERS

8.6.1 Soluble and Fusible Main Chain Liquid Crystalline Polymers

Amorphous polymers are soluble in suitable solvents at low temperature while crystalline polymers are soluble only at temperatures which sometimes are close to their melting point. The solubility of any polymer increases with the decrease of its ability to crystallize. A suppression of the melting temperature below the glass transition temperature (i.e., a kinetically prohibited crystalline phase) makes the corresponding polymer noncrystallizable. Therefore, since most rigid polymers have much higher glass transition temperatures than flexible polymers it is easier to decrease the crystallization tendency of the rigid polymers and therefore, make them soluble. This is also the case for main chain liquid crystalline polymers. A decrease of the melting transition temperature can be accomplished by raising G_k as shown in Figure 4. An increase in G_k can be accomplished by any synthetic technique which increases S , i.e. introduces structural defects in the polymer structure. Most conveniently, this is realized by copolymerization of a few monomers, addition of lateral substituents which provide a high configurational entropy (alkyl groups, *t*-butyl groups), insertion of flexible spacers, increasing the overall flexibility of the molecule and insertion of structural defects such as kinks, etc. The alternative solution is to increase both the glass

transition temperature of the polymer and its entropy simultaneously. In order to maintain a high ability towards mesophase formation the chemical reactions used to increase the solubility of the polymer should not disturb the ability of its backbone to generate a rod-like conformation. Therefore, the insertion of kinks or any other nonlinearities is not favorable since increases the solubility and decreases the ability to generate the mesophase. The ability to decrease the crystallization tendency is not so much related to the size of the lateral substituent as it is to the number of different configurational and conformational structural units which can result from the monomer which contains the side group. In fact according to thermodynamic considerations a high entropy can be realized either by a chain containing a large number of different structural units with different small substituents or by a chain containing in each structural unit a single substituent which yields a large number of conformers. The second situation, however, reduces drastically the interchain interactions and therefore, suppresses not only the ability towards crystallization but also the ability to generate a conventional liquid crystalline phase. Therefore, the most profitable synthetic technique is to use the copolymerization of few monomers containing small substituent with different electronegativities and ability to generate more than one constitutional isomeric structural unit from each monomer. Various research groups have used these principles, although in a non-systematic way, and accomplished fusible and soluble polymers. In the following subchapters we will enumerate only selected examples of polymers whose melting temperatures were lowered and therefore, were solubilized by using these principles.

8.6.1.1 *Poly(p-phenylene) and Its Derivatives*

The first soluble oligo(p-phenylene)s were synthesized by placing methyl substituents on the phenyl ring (Kern et al, 1960). The thermal behavior of these oligomers was first reported by Heitz (Heitz, 1986; 1989 A; 1991 A). These oligomers and their phase transitions are outlined in Scheme 1. After substitution, their solubility increases (Kern et al, 1960) and their melting points decrease. Methyl substituted oligo(p-phenylene)s have an axial ratio (x) equal to 0.8 times the number of benzene rings. According to theoretical predictions hexamethylsexiphenyl which has $x = 4.8$ and lower oligomers should not exhibit an enantiotropic mesophase. This is indeed the case. Octamethyloctaphenyl which has $x = 6.4$ and longer oligomers (i.e. those with x larger than the critical value $x = 6.2$) should and indeed display an enantiotropic nematic phase. Insertion of meta linkages suppresses their ability to form a mesophase (Scheme 1).

Soluble poly(p-2,5-di-n-alkylphenylene)s were prepared by Ni-catalyzed coupling of 1,4-dibromo-2,5-di-n-alkylbenzene (Rehahn et al, 1989 A) and Pd(0)-catalyzed coupling of 4-dibromo-2,5-di-n-alkylbenzeneboronic acid (Rehahn et al, 1989 B; 1990 A; Wahlenkamp and Wegner, 1994; Wilteler et al, 1993) (Scheme 2). The high molecular weight polymers display liquid crystalline phases (Wahlenkamp and Wegner, 1994; Wilteler et al, 1993).

Soluble phenylated poly(p-phenylene)s were also synthesized by Ni(II) catalyzed polymerization of 2,5-dibromobiphenyl, and by anionic polymerization of 2-phenyl-1,3-cyclohexadiene followed by aromatization (Scheme 3) (Noll et al, 1990). Most probably, both synthetic methods lead to regioregular phenylated

poly(p-phenylene)s. The high molecular weight polymer fractions exhibit an enantiotropic nematic mesophase.

Regioirregular substituted poly(p-phenylene)s were synthesized from substituted hydroquinones via Ni(0) catalyzed homocoupling of their bistriflates (Scheme 4) (Percec et al, 1992 J). All these polymers are soluble in conventional solvents, and many of them display liquid crystalline phases.

Other synthetic methods for the preparation of poly(p-phenylene)s were reviewed (Percec and Tomazos, 1992 Q; Schlüter and Wegner, 1993; Tour, 1994). Systematic research is still required to design poly(p-phenylene)s with liquid crystalline properties.

8.6.1.2 Metal Containing Poly(yne)s

Metal containing poly(yne)s are a relatively new class of rigid rod-like polymers. They can be prepared by a copper chloride-triethylamine catalyzed coupling of the appropriate metal halide with a dialkyne (Scheme 5) (Takahashi et al, 1982 A; 1984). A review on their synthesis is available (Hagihara et al, 1980). These polymers exhibit lyotropic liquid crystalline phases (Abe et al, 1991; Takahashi et al, 1982 B). Recently, two novel methods for the synthesis of this class of polymers were reported. The first one consists of the reaction of bis-trimethylstannyl(acetylide)s with trans-[M(PBu₃)₂Cl₂] (Davis et al, 1991), while the second one of the reaction of [Rh(PMe₃)₄Me] with diacetylenes (Chisholm, 1991; Fyfe et al, 1991) (Scheme 6). These metal containing poly(yne)s can be prepared with weight average molecular weights of up to 100,000 (Davis et al, 1991) and are therefore of interest both for their rigid rod-like character and for their

non-linear optical properties (Chisholm, 1991). Additional classes of metal containing liquid crystalline polymers were reviewed (Espinete et al, 1992; Giroud-Godquin and Maitlis, 1991; Hudson and Maitlis, 1993; Polishchuk and Timofeeva, 1993).

8.6.1.3 Spinal Columnar Liquid Crystalline Polymers

Dihydroxysilicon (IV) phthalocyanine can be condensed in solid state to yield insoluble phthalocyaninatopolysiloxanes (Orthmann et al, 1983; Orthmann and Wegner, 1986). However, octaalkyl substituted derivatives of dihydroxytin (IV) phthalocyanine (Sirlin et al, 1987), dihydroxysilicon (IV) octakis(dodecyloxymethyl)phthalocyanine (Sirlin et al, 1988 A; 1988 B) and octaalkoxy substituted silcondihydroxy phthalocyanines (Caseri et al, 1988; Sauer and Wegner, 1988) undergo polycondensation in liquid crystalline phase and yield soluble spinal columnar liquid crystalline polymers (Scheme 7). These polymers exhibit columnar hexagonal liquid crystalline phases which can range from -7 °C up to 300 °C (Sauer and Wegner, 1988; Sauer, 1993; Sirlin et al, 1987; 1988 A; 1988 B). The diameter of the column is determined by the length of the alkyl side groups (Sauer and Wegner, 1988; Sauer, 1993).

8.6.1.4 Aromatic Polyamides and Polyesters

Synthetic procedures for the preparation of soluble aromatic polyamides and polyesters were developed mostly by Gaudiana et al. (Gaudiana et al, 1987; Rogers et al, 1985 A; 1985 B; 1986; Sinta et al, 1987) Their research was recently reviewed (Gaudiana et al, 1989). Depending on their structure, these polymers can

be either amorphous or liquid crystalline (Gaudiana et al, 1989). A discussion of the influence of various molecular factors such as the position, polarizability and size of the substituents on the solubility of aromatic polyamides is available (Gaudiana et al, 1987; 1989). Table 2 (Gaudiana et al, 1987) summarizes some representative polymer structures. Their solubility is described in Table 3. An inspection of the structures from Table 2 and of the solubilities of these polymers presented in Table 3 suggests that the non-coplanar conformation of the biphenyl moiety (introduced by the presence of substituents in their 2,2'-positions), the statistical distribution of the biphenyl enantiomers, and the presence of structurally dissimilar diacids and diamines, all contribute to an enhanced solubility. A combination of these factors diminishes or even eliminates the interchain correlations necessary for close packing in crystals and may diminish Van der Waals forces of attraction. These orientation-dependent intermolecular attractive forces are important in the formation of all classes of liquid crystals (Flory, 1984 A; Flory and Matheson, 1984 B).

Soluble aromatic polyamides with a much lower solubility were also realized by attaching phenyl substituents either on the p-phenylene diamine or on the terephthalic acid monomer (Jadhav et al, 1988; 1989; Krigbaum et al, 1991). Some representative structures together with their solubilities are presented in Table 4 (Jadhav et al, 1988). All these polymers exhibit lyotropic liquid crystalline phases or at least melt before decomposition.

A reversible solubilization of poly(p-phenylene terephthalamide) was accomplished by the polycondensation of the chromium tricarbonyl complex of p-phenylenediamine with terephthaloyl chloride in N,N-dimethylacetamide (Dembek

et al, 1993; Jin and Kim, 1987). The polymer containing tricarbonyl chromium complexed structural units is soluble in dipolar aprotic solvents. Decomplexation can be achieved either by oxidation with I_2 or by heating above 150 °C.

Soluble poly(p-phenylene terephthalamide)s with phenyl and biphenyl units in the terephthalic acid were also synthesized (Hatke et al, 1991). The melting temperatures of these polymers were in the range of 440-490 °C and are overlapping their decomposition temperatures.

Aromatic polyamides containing alkyl side chains were reported (Ballauff, 1986 A; 1986 B; Ringsdorf et al, 1987; Schoenherr et al, 1986). When each structural unit contains four alkoxy groups, depending on their length, these polymers exhibit a board-like, "sanidic" mesophase (Ringsdorf et al, 1987; Schoenherr et al, 1986; Voight-Martin et al, 1995 A; 1995 B) (Figure 12). However, when there are only two alkoxy groups per one of the two monomeric units these polyamides display a new layered liquid crystalline mesophase (Ballauff, 1986 B; Ballauff and Schmidt, 1987). The corresponding polyesters containing four alkoxy groups in each monomeric unit or two alkoxy groups in only one monomeric unit display similar mesophases with the polyamides (Ballauff, 1986 B; Ballauff and Schmidt, 1987; Ringsdorf et al, 1987; Schoenherr et al, 1986; Voight-Martin et al, 1995 A; 1995 B).

Soluble aromatic polyesters were synthesized by using similar synthetic procedures with those employed in the polymerization of soluble aromatic polyamides. The research groups from Mainz reported on the solubilization of aromatic polyesters by the addition of alkyl side groups (Ballauff, 1986 B; Ballauff and Schmidt, 1987; Ringsdorf et al, 1987; Rodriguez-Parada et al, 1989;

Schoenherr et al, 1986; Voight-Martin et al, 1995 A; 1995 B). Solubility is easily accomplished for aromatic polyesters containing alkyl side groups when the alkyl groups derived from terephthalic acid monomer and respectively hydroquinone monomer are highly dissimilar in length (Rodriguez-Parada et al, 1989) (Scheme 8). For example the polyester from the top of Scheme 8, PTA16HQ-16, is highly crystalline and melts directly into an isotropic phase. However, PTA16HQ-6 exhibits much less crystallinity, is highly soluble and melts into a liquid crystalline phase. It is also instructive to compare the phase behavior of polyesters derived from bicyclo[2.2.2]octane-1,4-dicarboxylic acid with 2,5-dialkoxyhydroquinone diacetate (PBCOHQ-n) with those obtained from terephthalic acid and 2,5-dialkoxyhydroquinones (PTAHQ-n). Representative data on these polymers are available in Tables 5 and 6. As we can observe from the data reported in these Tables, all PTAHQ-n melt into a liquid crystalline phase while PBCOHQ-n melt directly into an isotropic phase. These results suggest that interchain interactions provided by the wholly aromatic backbone are necessary for the stabilization of a mesophase in this class of polymers (Rodriguez-Parada et al, 1989). Soluble homologues of poly(p-hydroxybenzoate) were also synthesized by attaching pendant alkyl groups (Stern et al, 1989). Thus, while poly(p-hydroxybenzoate) and poly(3-n-alkyl-4-hydroxybenzoate)s with alkyl groups shorter than six are only crystalline, the corresponding polymers with alkyl groups from six to sixteen are soluble and exhibit a thermotropic mesophase (Stern et al, 1989). It is interesting to mention that the polyesters with alkyl side groups display a layered mesophase which is different from the classic nematic or smectic mesophases exhibited by conventional rod-like polymers.

A large variety of soluble polyesters were prepared (Gaudiana et al, 1989; Sinta et al, 1987) by using the same synthetic principles as those used in the preparation of soluble polyamides.

A large group of soluble aromatic polyesters was prepared by attaching various large substituents such as phenylalkyl (Brugging et al, 1988; Vogel and Heitz, 1990), perfluoroalkyl (Freund et al, 1989), phenoxy and tert-butyl (Heitz and Niessner, 1990 A), phenyl and biphenyl (Heitz, 1991 A; 1991 B), or twisted biphenylene units such as 2,2'-dimethylbiphenylene (Classen et al, 1990; Schmidt and Guo, 1988), and 1,1'-binaphthyl-4,4'-ylene (Hohlweg and Schmidt, 1989). The dependence between the structure of various structural units and the solubility of the resulted polyesters was reviewed (Heitz, 1991 B; Heitz and Schmidt, 1990 B; Jin, 1994 A; Lee, K. S. et al, 1994; Schmidt, 1989; Teisler et al, 1994).

Tables 7 and 8 summarize the dependence between structure, thermal properties and solubilities of polyesters based on substituted hydroquinone and substituted terephthalic acid (Heitz and Schmidt, 1990 B; Hsiao et al, 1991; Kromer et al, 1991). The presence of dissimilar substituents on both monomers generates highly soluble polymers. Tables 9 and 10 show the dependence between the properties of polyesters obtained with twisted biphenyl monomers and their structure (Heitz and Schmidt, 1990 B; Hsiao et al, 1991; Kromer et al, 1991).

Nematic polyesters were obtained by the condensation of 2-phenylthioterephthalic acid, 2-(p-tolylthio)terephthalic acid, 2-(p-chlorophenylthio)terephthalic acid with the diacetates of hydroquinone, methylhydroquinone or 2,5-biphenyldiol (Kricheldorf et al, 1988 E). 2-(2-Naphthylthio)terephthalic acid was also used in conjunction with the same

bisnucleophiles to obtain noncrystallizable nematic copolyesters (Kricheldorf et al, 1988 F). The influence of various interconnecting groups present in the structure of bisphenols (i.e., O, CO, SO₂, S, C(CH₃)₂) on the phase behavior of polyesters with phenylthioterephthalic acid was also investigated (Kricheldorf and Erxleben, 1990 E). Similar polyesters were synthesized from phenoxyterephthalic acid (Kricheldorf et al, 1989 C), 4-fluoro-, 4-chloro-, 4-bromo-, 4-phenyl-, 4-cyclohexyl-, 4-phenoxy- and 4-cumyl- phenol (Kricheldorf and Engelhardt, 1990 A) with hydroquinone or 4,4'-biphenyldiol. The influence of the various polyesterification reaction conditions on the final structure and properties of polymers was also investigated. The synthetic methods used most frequently are outlined in Scheme 9 (Kricheldorf et al, 1988 A; 1989 C; Kricheldorf and Engelhardt, 1990 A).

For example the acetate method results in partial debromination of 4-bromophenoxyterephthalic acid units during their condensation with hydroquinone diacetate but not during the polymerization via the other two methods (Kricheldorf and Engelhardt, 1990 A) (Scheme 9). Model reactions have shown that both phenoxyterephthalic acid and its acid chloride yield anthrone-3-carboxylic acid above 180 °C and this product terminates the polymer chain end (Kricheldorf et al, 1988 A) (Scheme 10). This reaction is less probable when the acid chloride is reacted with the silylated hydroquinone. The interest in aryloxy- and arylthiosubstituted terephthalic acid was mainly determined by their convenient synthesis from dimethyl nitroterephthalate via aromatic nucleophilic displacement with the corresponding phenolate or thiophenolate.

Recently, the influence of the regioregularity on the solubility and thermotropic properties of main chain polyesters was investigated (Jin, J. L. et al, 1994 B). Soluble liquid crystalline aromatic polyesters were also synthesized from terephthalic acid derivatives, tert-butylhydroquinone and aromatic hydroxyfunctional polystyrene macromonomers (Heitz et al, 1989 B). The number average molecular weight of polystyrene side chains varied from 1000 to 2000 (Scheme 11). The resulting polyesters contain polystyrene grafts and are of interest as emulsifiers for nematic aromatic polyesters with polystyrene (Heitz et al, 1989 B). A graft copolymer containing a polyester main chain and polymethylmethacrylate graft units was synthesized from a hydroquinone substituted with polymethacrylate, t-butyl hydroquinone and bromoterephthaloyl chloride (Heitz et al, 1991 C). The hydroquinone containing polymethylmethacrylate substituent was prepared by group transfer polymerization (Scheme 12). Block copolymers containing thermotropic polyester and glassy polystyrene segments were also reported (Galli et al, 1994).

8.6.1.5 Rod-Like Soluble Polyimides

Rigid rod-like polyimides were synthesized by the sequence of reactions presented in Schemes 13 and 14 (Metzmann et al, 1989; Wenzel et al, 1987). The series of polymers from Scheme 13 contain alkyl side groups (Wenzel et al, 1987) while the one from Scheme 14 contain oligooxyethylene side groups (Metzmann et al, 1989). The merit of these two synthetic schemes is that the resulting polymers contain only imide rings. Soluble polyimides were also reported by the conventional sequence of reactions from Scheme 15 (Duran et al, 1988). All these

rigid rod-like polyimides form layered mesophases (Duran et al, 1988; Metzmann et al, 1989; Wenzel et al, 1987). It is interesting to mention that polymers containing identical length of their alkyl side groups are isomorphic within their crystalline phase and therefore, form solid solutions regardless of the nature of their polymer backbone (Duran et al, 1988). For example the polyimide from the top part of Scheme 15 is isomorphic with the polyester which has an identical number of carbons in its side groups (bottom part of Scheme 15) (Duran et al, 1988).

Soluble polyimides were also synthesized from 3,6-diphenylpyromellitic dianhydride with various diamines (Harris and Hsu, 1989). A lyotropic polyimide was obtained from the twisted 2,2'-bis(trifluoromethyl)-4,4'-diaminobiphenyl and 3,6-diphenylpyromellitic dianhydride (Scheme 16) (Harris and Hsu, 1989). A brief review on liquid crystalline polyimides is available (Kricheldorf, 1994).

8.6.1.6 Thermotropic Poly(1,4-arylenevinylene)s

Poly(phenylenevinylene)s can be synthesized by a variety of reactions including Wittig reaction (Horhold and Opfermann, 1970; Horhold et al, 1987; Kossmehl and Samandari, 1985), Hofmann elimination (Antoun et al, 1986), McMurry reaction (Cooke and Wagener, 1991; Feast and Millichamp, 1983; Rehahn, 1990 B), Heck reaction (Heitz et al, 1988) and Siegrist reaction (Kretzschmann and Meier, 1991; Siegrist, 1981).

Liquid crystalline oligo(p-phenylenevinylene)s were first reported by Campbell and McDonald (Campbell and MacDonald, 1959). High molecular weight poly(p-phenylenevinylene)s are insoluble and infusible. The first thermotropic poly(phenylenevinylene)s were recently reported (Memeger, Jr.,

1989). They were synthesized by the Wittig reaction. The insertion of suitable substituents such as Cl on the phenyl ring, the replacement of phenyl rings with anthracene or naphthalene and of vinylene with ethane allowed the synthesis of thermotropic poly(arylenevinylene)s (Memeger, Jr., 1989).

Thermotropic poly(arylenevinylene)s were also synthesized by various synthetic methods based on the Heck reaction (Brenda et al, 1990; Greiner and Heitz, 1988; Heitz, 1991 B; Heitz et al, 1988). Some of these procedures are outlined in Scheme 17. The highest solubility is obtained with the polymer with $R_1=H$ and $R_2=C_6H_5$. The polymers with $R_1=H$ and $R_2=C_6H_5$ or CF_3 exhibit thermotropic mesophases (Greiner and Heitz, 1988). Additional examples of poly(p-arylene vinylene)s are presented in Scheme 18 (Martelock et al, 1991). As expected, copolymers with highly dissimilar structural units which can also yield constitutional isomeric structural units yield soluble, thermotropic liquid crystalline polymers which are conjugated (Martelock et al, 1991). Only qualitative information is available on their liquid crystalline behavior. Thermotropic poly(phenylenevinylene)s containing flexible spacers were also synthesized by the Heck reaction (Suzuki et al, 1990). More recently liquid crystalline poly(p-phenylene vinylene)s were obtained by the Heck coupling of p-divinylbenzene with 1,4-dialkyloxy-2,5-diiodobenzene (Bao et al, 1993).

8.6.1.7 Other Conjugated Polymers

Alternating copolymers such as poly(1,4-phenylene-2,5-thiophene) were prepared by the Stille cross-coupling reaction. When the 1,4-phenylene repeat units contain 2,5-dialkyloxy substituents, these conjugated copolymers exhibit nematic

mesophases (Yu et al, 1993). Both α -sexithienyl (Destri et al, 1993) and poly(α -hexathiophene) (Qian et al, 1994) were recently shown to display a nematic mesophase.

8.6.1.8 Polyurethanes

Thermotropic polyurethanes were reported beginning with 1981 (Iimura et al, 1981; Tanaka and Nakaya, 1984; 1986; 1987; 1988). Most of them were thermally unstable in their liquid crystalline phase. The first examples of thermally stable polyurethanes were reported by Kricheldorf et al. (Kricheldorf and Awe, 1988 D; 1989 E; Kricheldorf and Jenssen, 1989 A) Smectic polyurethanes were synthesized from the bischloroformates of 4,4'-alkylenedioxydiphenols with piperazine, trans-2,5-dimethylpiperazine and 4,4'-bipiperidine by interfacial polycondensation (Scheme 19) (Kricheldorf and Awe, 1989 E). Polyurethanes without flexible spacers were synthesized from 4,4'-bipiperidine, 1,2-bis(4-piperidinyl)ethane and 1,3-bis(4-piperidinyl)propane with the bischloroformates of p-phenylene, 2-methyl-1,4-phenylene or 2,5-bisphenylene. Copolyurethanes were also synthesized (Kricheldorf, 1989 F). The polymers derived from hydroquinone or methylhydroquinone are semicrystalline with short-term stability up to 310 °C. The polymers obtained from phenylhydroquinone are amorphous with a thermal stability up to 360 °C. Polyurethanes and copolyurethanes prepared from 4,4'-biphenylene units form a smectic layered structure and a nematic mesophase. While the research group of Kricheldorf decreased the crystallization ability of polyurethanes by suppressing the hydrogen bonding ability of the urethane groups, Mormann et al. have generated thermally stable polyurethanes

from diisocyanates of substituted phenyl benzoates (Mormann and Hissmann, 1987; Mormann and Brahm, 1989 A; 1990 B; 1991 B; Mormann and Hohn, 1989 B; Mormann and Baharifar, 1990 A; Mormann and Benadda, 1991 A; Mormann et al, 1995). The resulted polyester-urethanes are more flexible and generate a broader range of mesophase by decreasing the melting temperature (Mormann and Benadda, 1991 A; Mormann and Brahm, 1991 B). Additional examples of polyurethanes were reported by MacKnight et al (Stenhouse et al, 1989). Recently liquid crystalline polyurethanes with mesogenic side groups were reported (Koide et al, 1994).

8.6.1.9 Polycarbonates

The first examples of polycarbonates containing flexible spacers were reported by Roviello and Sirigu (Roviello and Sirigu, 1979; 1980) and by Sato et al (Sato et al, 1986; 1988). Poly(ester carbonate)s from tert-butylhydroquinone and terephthalic acid were first reported by Prevorsek et al (Lai et al, 1988). Soluble aromatic copolycarbonates were synthesized by Kricheldorf and Lubbers (Kricheldorf and Lubbers, 1989 D; 1990 B). They are conveniently prepared by copolymerization of three or four bisphenols with bis(trichloroacetyl)carbonate. For example, copolycarbonates based on 4,4'-dihydroxybiphenyl, methylhydroquinone and 4,4'-dihydroxybiphenyl ether or 4,4'-dihydroxybenzophenone are soluble in aprotic organic solvents such as methylene chloride (Kricheldorf and Lubbers, 1990 B). Poly(ester carbonate)s were also synthesized by melt polycondensation of substituted hydroquinones and diphenylterephthalate with diphenylcarbonate (Lai et al, 1990) and from p-

hydroxybenzoic acid, 4,4'-dihydroxybiphenyl and diphenylcarbonate (Kawabe et al, 1990).

8.6.1.10 Poly(ester anhydride)s

Thermotropic poly(ester anhydride)s were synthesized from terephthaloyl chloride with silylated hydroxy acids (Kricheldorf and Lubbers, 1990 D). The polymers presented in Scheme 20 are noncrystallizable and exhibit a nematic phase over a broad range of temperatures (Kricheldorf and Lubbers, 1990 D).

8.6.1.11 Poly(ester imide)s

Thermotropic poly(ester imide)s were developed by Kricheldorf's group. The first series of thermotropic poly(ester imide)s were synthesized starting from trimellitic anhydride and α,ω -diaminoalkanes containing from four to twelve methylene units. The resulting α,ω -diaminoalkane bis(trimellitimide)s were reacted with various 4,4'-diacetoxybisphenols (Scheme 21) including those based on 4,4'-dihydroxybiphenyl (Kricheldorf and Pakull, 1988 B), hydroquinone, methyl-, chloro-, phenyl- and tetrachlorohydroquinone, 1,5-, 1,4-, 2,7- and 2,6-dihydroxynaphthalenes (Kricheldorf and Pakull, 1987 B). All these polymers crystallize in a layered structure. The polymers with Ar = 4,4'-biphenyl melt into a smectic mesophase (Kricheldorf and Pakull, 1988 B). The melting temperature varies from 297 °C for the polymer with n = 12 to 393 °C for the polymer with n = 4. The liquid crystalline phase undergoes isotropization at 386 °C for the polymer with n = 12 and at 467 °C for the polymer with n = 4. The rate of crystallization of all these polymers is unusually fast. With the exception of the polymers based on

Ar = 1,4-phenylene, 1,4-tetrachlorophenylene and 2,6-naphthalene, which exhibit a smectic mesophase, the other polymers melt directly into an isotropic phase (Kricheldorf and Pakull, 1987 B).

The second procedure used in the preparation of poly(ester imide)s is based on the reaction of pyromellitic dianhydride or benzophenone-3,3',4,4'-tetracarboxylic dianhydride with aminoacids or lactams followed by the condensation of the resulting diacids with diacetates of hydroquinone, 2,6-dihydroxynaphthalene or 4,4'-dihydroxybiphenyl (Kricheldorf et al, 1988 C). All these polymers crystallize in a layered structure. With the exception of the polymer with $n = 11$, all the other polymers based on Ar = 4,4'-biphenyl exhibit a smectic mesophase. The polymer with $n = 10$ and Ar = 1,4-phenylene exhibits a smectic mesophase. The other polymers based on Ar = 1,4-phenylene or 2,6-naphthylene melt directly into an isotropic phase (Kricheldorf et al, 1988 C).

An additional method for the synthesis of thermotropic poly(ester imide)s is based on the reaction of trimellitic dianhydride with aminoacids or lactams followed by condensation with acetates of bisphenols (Scheme 22). This reaction can be performed as "one pot procedure" (Kricheldorf et al, 1989 B). Again all homopolymers exhibit a lamellar crystalline phase which in all cases melts into an enantiotropic smectic phase. However, the corresponding copolymers exhibit a nematic mesophase. It is interesting to mention that the homopoly(ester imide)s from Scheme 22 are in fact copolymers since their structural units have two constitutional isomers. Finally, fully aromatic poly(ester imide)s were reported by the same research group by using several different synthetic procedures which are outlined in Scheme 23 (Kricheldorf and Pakull, 1985; 1989 G; Kricheldorf et al,

1989 H; Kricheldorf and Huner, 1990 C). The imide monomers from Scheme 23 were homopolymerized and copolymerized either between themselves or with other aromatic dicarboxylic acids, bisphenols or hydroxyacids to give fully aromatic poly(ester imide)s with complex thermal behavior (Kricheldorf and Pakull, 1989 G; Kricheldorf et al, 1989 H). However, the fully aromatic poly(imide ester)s from Scheme 24 exhibit glass transition temperatures between 140 and 180 °C and nematic mesophases which undergo isotropization between 375 and 500 °C (Kricheldorf and Huner, 1990 C).

8.6.1.12 Polyhydrocarbons

In addition to the class of poly(arylenevinylene)s described in chapter 8.6.1.6 and poly(phenylene)s and poly(arylene)s described in chapter 8.6.1.1 liquid crystalline polymers containing rigid rod-like mesogens and flexible spacers and based only on carbon-carbon bonds were also synthesized by the homocoupling of bis(4-bromophenyl)alkanes (Sung et al, 1990).

8.6.1.13 Polyethers

Thermotropic polyethers based on rigid rod-like mesogens and flexible spacers are of interest since they do not undergo transesterification or other rearrangement reactions during their characterization which requires extensive annealing at high temperatures. The effect of thermally induced rearrangement reactions will be discussed in a subsequent chapter. Polyethers can be conveniently prepared by the phase transfer catalyzed polyetherification of mesogenic bisphenols with α,ω -dibromoalkanes. The main criterion required for their synthesis is good

solubility of the resulting polymer in the reaction medium (Percec, 1988 B; 1988 C; Percec et al, 1991 L; 1991 M).

8.6.1.14 Liquid Crystalline Fluorocarbon-Hydrocarbon Copolymers

Main chain fluorocarbon-hydrocarbon alternating copolymers were synthesized by radical initiated addition of α,ω -diiodoperfluoroalkanes to α,ω -alkanedienes, followed by the reduction of the secondary iodide groups with Bu_3SnH (Davidson et al, 1995; Wilson and Griffin, 1993). Since hydrocarbon and fluorocarbon segments are highly immiscible, these "*microblock*" copolymers form lamellar structures which display smectic B mesophases.

Semifluorinated main chain polyesters based on aliphatic dicarboxylic acids and aliphatic diols, one being perfluorinated while the other perhydrogenated, also exhibit a thermotropic smectic B phase (Wilson, 1994 A; 1995).

Polyesters with hydrogenated backbones and fluorinated paraffinic side groups display smectic A and B phases (Wilson and Griffin, 1994 C; 1994 D).

8.6.2 Persistence Lengths of Soluble Main Chain Liquid Crystal Polymers

The persistence length and the Mark-Houwink coefficient, a , were determined both for soluble polyesters and polyamides. For soluble polyesters the persistence length data obtained by various authors are 95 Å ($a=0.95$) (Heitz and Schmidt, 1990 B), 120 ± 10 Å ($a=0.85$ but estimated to be 1.0) (Kromer et al, 1991), and 110 Å ($a=1.0-1.1$) (Hsiao et al, 1991). For substituted aromatic polyamides the values of the persistence length reported are 85 ± 26 Å (Krigbaum et

al, 1991) and 200 Å ($a=1.1-1.2$) (Gaudiana et al, 1989). Both values are lower than those reported for poly(p-phenylenediamine terephthalic acid) (150-290 Å) and for poly(p-benzamide) (240-750) Å (Krigbaum et al, 1991). All these results demonstrate that both polyesters and polyamides do not resemble rigid rods but are comparable to typical semiflexible chains. In addition, the values obtained for the Mark-Houwink coefficient, a , also support the semiflexible character of these chains (a is 0.8 for flexible and 2.0 for rigid chains). While aromatic polyamides, depending on substituent, can generate lyotropic solutions, soluble polyesters do not. Films cast from solutions of aromatic polyesters are transparent (amorphous) and become turbid (anisotropic) only after annealing above their glass transition temperature. In conclusion, although due to interchain interactions the rigidity of polyesters and polyamides increases versus that predicted by gas phase and dilute solutions of low molar mass compounds, both types of polymers belong to the class of semiflexible polymers. A recent discussion on the persistence length of polyesters, polyamides, polyimides and even poly(p-phenylene)s concludes that truly rigid rod polymers may not become available from one dimensional chains (Tiesler et al, 1994).

8.7 CHEMICAL HETEROGENEITY IN MAIN CHAIN LIQUID CRYSTALLINE COPOLYMERS

As discussed in chapter 8.6, main chain liquid crystalline polymers and copolymers are synthesized by step polymerizations that are based on reversible or irreversible reactions. A polymerization reaction is reversible depending on its mechanism and on the reaction conditions used. In contrast to chain

copolymerizations, step copolymerizations performed in a homogeneous phase at high conversion and with a stoichiometric ratio between comonomers always lead to copolymer compositions that are identical with the comonomer feed. Also, the difference between the reactivities of various monomers used in step reactions is lower than in the case of monomers used in chain reactions. This implies that the compositional heterogeneity of the copolymers obtained by step reactions is lower than that of copolymers synthesized by chain copolymerizations where copolymer composition is conversion dependent. However, again in contrast to chain copolymerizations, in step copolymerizations the copolymer's sequence distribution can be either kinetically (in irreversible copolymerizations) or thermodynamically (in reversible copolymerizations) determined. In reversible step copolymerizations, the sequence distribution is thermodynamically controlled and the copolymer microstructure is determined by redistribution reactions. The copolymer sequence distribution (Chen and Lenz, 1985; Lenz et al, 1983) and the configuration of the structural units (Irwin et al, 1989; Gardner et al, 1988; Kricheldorf and Schwarz, 1987 A; Kwolek and Louise, 1986) are both determined by the type of phase (isotropic, liquid crystalline, or crystalline) in which copolymerization or the copolymer reorganization reaction is performed. Microheterogeneous copolymerization reactions complicate the control of the copolymer's microstructure since the concentration of the comonomers in the proximity of the growing chain is determined by the miscibility and/or the association between the growing chain and the monomers. The concept that the growing chain can control its own environment during copolymerization was explained on the basis of the "bootstrap" model and its implications were recently reviewed (Harwood, 1987). Some of the

most recent examples of "bootstrap effects" were observed in the radical copolymerization of macromonomers (Mülbach and Percec, 1987; Percec and Wang, 1990 A; 1992 O), in the synthesis of block copolymers from immiscible amorphous segments, (Auman et al, 1987 A; 1987 B) and in the synthesis of ternary copolymers from monomers that can give rise to amorphous and liquid crystalline structural units by reversible copolymerization reactions (Auman and Percec, 1988).

Copolymerization reactions performed in bulk are frequently used in the preparation of liquid crystalline polyesters, poly(ester imide)s, etc. The starting monomers lead to isotropic melts, nevertheless above a certain conversion this reversible reaction is performed in the liquid crystalline phase. A heterogeneous composition is generated both by the different reactivities of the monomers and by the polydispersities of the polymers. This heterogeneous composition generates a microphase separated reaction mixture which at a given temperature contains isotropic, liquid crystalline and crystalline phases. Each of these phases generates a polymer homologous series of copolymers which have both different compositions and for the same composition a different sequence distribution. The sequence distribution is determined by the phase in which the copolymer is generated i.e., isotropic, liquid crystalline or crystalline. This microheterogeneous copolymerization reaction enhances the chemical heterogeneity of the resulted copolymers. Both the polydispersity and the chemical heterogeneity of liquid crystalline copolymers are responsible for the biphasic or even multiphasic nature of liquid crystalline copolyesters (D'Allest et al, 1986; Economy, 1990 A; 1990 B; Laus et al, 1991; Martin and Stupp, 1988; Moore and Stupp, 1988; Ober et al,

1990; Stupp et al, 1988). The chemical heterogeneity of liquid crystalline copolymers is reduced or even eliminated in the case of azeotropic irreversible copolymerizations (Percec and Tsuda, 1990 B; 1991 R; Sherwood et al, 1994). Excellent discussions on the change in sequence distribution and molecular weight during the annealing of thermotropic polyesters is available (Economy, 1990 A; Economy et al, 1990 B; MacDonald et al, 1991). The same processes should take place in polyamides, polycarbonates, poly(ether imide)s, polyurethanes, polyanhydrides and any other polymers containing chemical bonds which can undergo rearrangement reactions during thermal treatment.

8.8 FLEXIBLE AND SEMIFLEXIBLE LIQUID CRYSTALLINE POLYETHERS

Flexible liquid crystalline polyethers are based on flexible mesogenic units which are rod-like mesogenic units based on conformational isomerism. In gas phase and dilute solution these units are as flexible as n-butane (Percec and Zuber, 1991 O) (see chapter 8.4.2). However, in melt phase interchain interactions are increasing their rigidity. The simplest structural units which can be used for the synthesis of flexible liquid crystalline polymers based on conformational isomerism are diphenylethane, phenylbenzyl ether, and methyleneoxy units (Scheme 25). Flexible rod-like mesogens or rod-like mesogens based on conformational isomerism exhibit a number of different conformers which are in dynamic equilibrium. The two most stable conformers are the anti and gauche. The anti conformer has an extended rod-like shape and therefore is expected to display liquid crystallinity. The gauche conformer is similar to a "kinked" unit which is

occasionally introduced within the structure of main chain liquid crystalline copolymers based on rigid rod-like mesogens to decrease their crystallization ability. Therefore, the insertion of flexible units capable of giving rise to extended and kinked conformers within the main chain of a polymer is expected to provide a liquid crystalline polymer having a dynamic composition. To date there are no data on the dynamic equilibrium between different conformers of "flexible" rod-like mesogens. However, it is well established that when rod-like or linear conformations are in dynamic equilibrium with random-coil conformations, the rod-like conformation is preferred in the nematic phase (deGennes and Pinkus, 1977; Flory and Matheson, 1984 B; Kim and Pinkus, 1979). Therefore, it is not excluded that in the nematic phase the preferred conformer may be the anti.

Low molar mass liquid crystals based on benzyl ether and diphenylethane units are well known. Table 10 summarizes the dependence between the structure of some benzyl ether compounds and the thermodynamic stability of their mesophase. A brief inspection of this Table shows that all flexible compounds listed exhibit liquid crystalline mesophases. However, the thermodynamic stability of their mesophase with respect to the crystalline phase is drastically dependent on subtle changes in their structure. For example compound 1 exhibits a virtual nematic mesophase at -20°C . Hydrogenation of one of its phenyl rings enhances its isotropization by 68.6°C . Nevertheless, the nematic phase of compound 2 is only monotropic. The replacement of the 1,4-cyclohexane ring of 2 with a bicyclooctane unit generates an enantiotropic mesophase. The difference between the isotropization temperature of compounds 1 and 3 from Table 10 is 93°C . If we replace the cyano group of 2 with a pentyl group the new compound 4 exhibits

again a virtual mesophase. The replacement of a methylenic unit of the pentyl group of 4 with an oxygen generates compound 6 which displays a monotropic nematic phase. The substitution of the methyleneoxy group of 6 with an ethane unit generates an enantiotropic nematic mesophase (compound 7).

Table 11 provides some examples of low molar mass liquid crystals based on diphenylethane, cyclohexylphenylethane, dicyclohexylethane and dicyclooctylphenylethane (Carr et al, 1983; Carr and Gray, 1985; Kelly and Schad, 1984; Osman, 1982 A; 1982 B; Osman and Ba, 1983; Praefke et al, 1980; Schadt et al, 1983). The flexible mesogenic units from Table 11 follow the same trend as those from Table 10. For example the phase behavior of 1 and 2 from Table 10 is almost identical to that of 8 and 9 from Table 11. Hydrogenating a phenyl ring from 8 increases the thermal stability of the nematic phase of 9 by about 75 °C versus that of 8. Replacing a phenyl ring from 8 with a bicyclooctane ring enhances the thermodynamic stability of the nematic phase by 137 °C.

Let us now consider that we increase the molecular weight of 1 or 8 by polymerization. According to the thermodynamic trends discussed in chapter 8.5.3, the virtual mesophase of the monomeric structural unit should become at higher molecular weights enantiotropic, monotropic or remain virtual. In the last case the transition of the virtual mesophase of the polymer should however be shifted to higher temperatures.

The synthesis of the first flexible main chain liquid crystalline polyether without spacers is outlined in Scheme 26 (Percec and Yourd, 1988 A). As expected based on the above discussion, the resulted polyethers based on trans 1,4-bis[(methylsulfonyl)methyl]cyclohexane and methylhydroquinone or

phenylhydroquinone display an enantiotropic nematic mesophase. The copolymers containing also some amount of cis 1,4-bis[(methylsulfonyl)methyl]cyclohexane also display a nematic mesophase. DSC traces of the polyethers based on methylhydroquinone and trans 1,4-bis[(methylsulfonyl)methyl]cyclohexane are identical to those of the corresponding polyesters based on methylhydroquinone and 1,4-cyclohexanedicarboxylic acid (Kricheldorf and Schwarz, 1987 A; Kwolek and Louise, 1986; Kyotari and Manetsuna, 1983) except that the phase transitions of the polyethers are shifted to lower temperatures (Percec and Yourd, 1988 A). Based on the thermodynamic principles discussed previously this is an expected result since the corresponding polyesters are identical to the polyether from Scheme 26 except that the methyleneoxy units from the structure of the polyethers are replaced with ester units. This increases only the overall rigidity of the polyesters versus that of the polyethers.

Polyethers based on substituted hydroquinones and p-dibromo- or dichloroxylylene also lead to liquid crystalline polyethers (Memeger, 1991).

Memeger (Memeger, 1991) has synthesized in 1975 high molecular weight polyethers based on α,α' -dichloro-p-xylene and methylhydroquinone in dimethylacetamide using K_2CO_3 as base. Fibers with high modulus (233 g/denier) were spun from these polymers. Unfortunately the polyetherification of substituted hydroquinones with α,α' -dichloro-p-xylene leads both to C- and O-alkylation reactions. Nematic polyethers with and without flexible spacers were also synthesized by cationic ring opening polymerization of exo-2-methyl-7-oxabicyclo[2.2.1]heptane and 7-oxabicyclo[2.2.1]heptane as well as by the

copolymerization of the later monomer with tetrahydrofuran and/or ethylene oxide (Kops and Spanggaard, 1986; Sikkema and Hoogland, 1986) (Scheme 27).

A comprehensive series of experiments was performed with polyethers based on 1-(4-hydroxyphenyl)-2-(2-R-hydroxyphenyl)ethane (RBPE) and α,ω -dibromoalkanes containing from four to twenty methylenic units (Percec and Tsuda, 1989 N; 1989 O; 1990 B; 1990 D; 1990 H; 1991 Q; 1991 R; Percec and Yourd, 1989 D; 1989 I; 1990 E; 1990 G; Ungar et al, 1990), particularly those based on 1-(4-hydroxyphenyl)-2-(2-methyl-hydroxyphenyl)ethane (MBPE). All these polyethers are in fact copolyethers since their structural unit has two constitutional isomers (Scheme 28). With the exception of MBPE-5 and MBPE-9 which exhibit two monotropic nematic mesophases, and MBPE-8 and MBPE-11 which exhibit one monotropic nematic mesophase, all the other MBPE-X polyethers are only crystalline (Percec, 1990 D). Nevertheless, again based on the thermodynamic discussion from chapter 8.5 we can assume that all of them may exhibit virtual mesophases. The virtual transition temperatures and thermodynamic parameters of all MBPE-X polymers were determined by copolymerization experiments of MBPE with two different flexible spacers (Percec and Tsuda, 1989 N; 1989 O; 1990 B; 1990 D; 1990 H; 1991 Q; 1991 R; Percec and Yourd, 1988 A; 1989 D; 1989 I; 1990 F; 1990 G; Ungar et al, 1990).

The technique developed and used for the determination of their virtual transition temperatures and thermodynamic parameters is as follows. The structural units of the copolymers resulted from two flexible spacers and one mesogen are isomorphic in their mesophase but not in their crystalline phases. As a consequence, the crystallization temperature of the copolymer is decreased and

exhibits an eutectic point while both the temperature and the enthalpy associated with the mesophase are displaying continuous dependences on composition. Therefore, in the mesophase the two structural units behave as an ideal solution and obey the Schroeder-Van Laar equations (chapter 8.3) (Achard et al, 1989; Schroeder, 1893; Van Hecke, 1979; Van Laar, 1908). Since the difference between ΔH_1 and ΔH_2 of the two homopolymers is not large and the values of ΔH_1 and ΔH_2 are proportional to their T_1 and T_2 transition temperatures most of these dependences are linear. Therefore, upon extrapolation to the composition of the two homopolymers the "uncovered" temperature transitions of the copolymers can be used to determine both virtual transition temperatures and their associated thermodynamic parameters of the parent homopolymers. An example of DSC traces for the copolymer MBPE-5/8 (i.e. based on five and eight methylenic units in the spacer) is presented in Figure 13. The dependences of transition temperatures and enthalpy changes of MBPE-5/8 versus composition for the results collected from Figure 13 together with their extrapolations are presented in Figure 14 (Percec and Yourd, 1990 G). The virtual phase transition temperatures and thermodynamic parameters of MBPE-X determined from various pairs of flexible spacers agree very well (Percec and Tsuda, 1990 D). Figure 15 presents the plot of the dependence of the virtual isotropic-nematic transition temperatures as a function of the number of carbons (x) in the flexible spacer and its inverse ($1/x$) (Percec and Tsuda, 1990 D). We can observe from Figure 15 that the virtual mesophase of these polymers does not vanish even at very long spacer length. This suggests that polyethylene should also exhibit a virtual mesophase as was indeed theoretically predicted (Ronca and Yoon, 1982). The highest temperature nematic mesophase of

MBPE-X homopolymers and copolymers was confirmed by X-ray experiments (Cheng et al, 1991; Ungar et al, 1990). The entire series of ClBPE-X homopolymers behaves almost identical to the series of MBPE-X polymers and confirms all these data (Zuber, 1991).

The thermodynamic parameters associated with the isotropic-nematic phase transition temperatures of MBPE-X (Percec and Tsuda, 1990 D) and ClBPE-X were plotted as a function of the number of carbons in the spacer and the orientational contribution of the mesogen and conformational contribution per $-\text{CH}_2-$ group at the isotropic-nematic transitions were determined (Percec and Tsuda, 1990 D; Zuber, 1991). These values are summarized in Table 12 together with the corresponding data obtained for the polyethers based on 4,4'-dihydroxy- α -methylstilbene (HMS-X) (Percec et al, 1991 M) and of the polyesters based on 4,4'-dihydroxy-2,2'-dimethylazoxybenzene and α,ω -alkanedioic acids (DMAB-X) (Blumstein and Blumstein, 1988). The polymers HMS-X and DMAB-X contain rigid rod-like mesogens, while MBPE-X and ClBPE-X contain flexible rod-like mesogens. As we can see from Table 12 both the enthalpic and entropic contributions per $-\text{CH}_2-$ are independent of the nature of the mesogen. They are higher for the polymers based on even spacers and all data are in good agreement. However, the orientational entropic contributions per mesogen are higher in the case of flexible mesogens than in the case of rigid mesogens. This result suggests that at the isotropic-nematic transition, the flexible mesogen undergoes in addition to the orientational arrangement also a transition from its gauche into its anti conformer.

The determination of the virtual phase transition temperatures of polymers can be also done by preparing mixtures with low molar mass liquid crystals or blends with other virtual liquid crystalline polymers. However, these two techniques are less reliable than the copolymerization based technique (Percec and Tsuda, 1991 Q).

It has been also shown that copolymerizations based on two and more than two flexible spacers or mesogenic units can be used to engineer phase transition temperatures and corresponding thermodynamic parameters of copolymers (Percec and Tsuda, 1990 B; 1991 R). The only requirement for these experiments is that the structural units of these copolymers should be isomorphic within the mesophase we want to tailor make and the molecular weight of the homopolymers and copolymers should be higher than the molecular weight below which phase transitions are molecular weight dependent. When the thermal transition temperatures and the corresponding enthalpy changes of the homopolymers are not highly dissimilar both the transition temperatures of the copolymers and their associated enthalpies can be calculated from Equations 4 and 5, in which X_n is the mole fraction of the structural unit n from copolymer and T and ΔH are the transition temperature and the enthalpy change associated with the same phase transition of the parent homopolymer based on an identical structural unit (Percec and Tsuda, 1991 R).

MBPE-X and ClBPE-X with $x = 5, 7, 9, 11$ and 13 exhibit a second uniaxial nematic mesophase which in certain polymers is monotropic while in other is virtual (Percec and Tsuda, 1990 D; Zuber, 1991). This second nematic mesophase was transformed into an enantiotropic one by copolymerization

experiments and was subsequently characterized by X-ray experiments (Ungar et al, 1992; 1994 B; 1995). This second uniaxial nematic phase was theoretically predicted (Ferrarini et al, 1993; Vasilenko et al, 1984).

The influence of the size of various substituents on the phase transitions of RBPE-X was also investigated (Percec and Zuber, 1992 H). It has been demonstrated that phase transition temperatures of polymers depend on the nature of lateral substituent by following the same trend as that followed by low molar mass liquid crystals. Some data are summarized in Table 13. A detailed discussion is available (Percec and Zuber, 1992 H). When the substituent of RBPE-X polymers is H, i.e. BPE, they do not exhibit anymore a nematic mesophase. For example, BPE-8/10 (i.e. the copolymer containing a 50/50 molar ratio of spacer lengths containing eight and ten carbon atoms) displays an enantiotropic *sb* mesophase (Ungar et al, 1991 B). At the same time, BPE-8/12 (i.e. the copolymer containing a 50/50 molar ratio of spacer lengths containing eight and twelve carbon atoms) exhibits an enantiotropic columnar hexagonal (Φ_h) mesophase (Ungar et al, 1991 A). By increasing the length of the mesogenic unit from BPE to 4,4'-bis[2-(4-hydroxyphenyl)ethyl]benzene (PEB) (Scheme 29), the resulting homopolyethers PEB-X and the copolyethers based on PEB, BPE and various flexible spacers all exhibit columnar mesophases (Percec et al, 1992 F; 1992 N). Both the phase transition temperatures and the corresponding thermodynamic parameters of the columnar hexagonal mesophases can be tailor made by similar copolymerization experiments (Percec et al, 1992 F; 1992 N) as those used to tailor make nematic mesophases (Percec and Tsuda, 1990 B; Ungar et al, 1990). The columnar hexagonal mesophase of BPE and PEB copolymers is not unexpected if we

consider them as being "copolymers" of polyethylene and poly(p-xylylene). Since both polyethylene and poly(p-xylylene) display a columnar hexagonal mesophase it is expected that RBPE-X with $R = H$ or even F to display the same mesophases (Ungar et al, 1991 A). Figure 16 outlines the columnar hexagonal phases of polyethylene, poly(p-xylylene) and of some of the copolymers based on BPE and PEB (Ungar et al, 1991 A). As we can observe from Figure 16 the columnar hexagonal mesophase is induced by the conformational disorder of the spacer.

So far, with few exceptions, all the experiments with polyethers based on RBPE generate mesophases which are either thermodynamically unstable (virtual) with respect to the crystalline phase or metastable (monotropic). Based on the thermodynamic discussion from chapter 8.5 an increase of the rigidity of the mesogen and a simultaneous increase in its disorder or entropy should decrease the ability towards crystallization and increase the ability towards the generation of a mesophase. Scheme 30 outlines the development of a series of polyethers based on this concept (Percec and Kawasumi, 1991 K). A 4-hydroxyphenyl group from BPE was replaced with 4-hydroxybiphenyl to increase its rigidity. The ethyl group from BPE was replaced with 1,2-butane group. Thus a new mesogenic group 1-(4-hydroxy-4'-biphenyl)-2-(4-hydroxyphenyl)butane (TPB) results (Percec and Kawasumi, 1991 K). TPB has a chiral center and therefore the racemic monomer leads to TPB-X "copolymers" based on four constitutional isomeric structural units (Scheme 30). These polymers are soluble in conventional solvents. The phase transitions of TPB-X (with $X = 4$ to 20) are summarized in Figure 17 (Percec and Kawasumi, 1991 K). The dependences of glass transition, isotropization and melting transition temperatures versus x are different and as a consequence, they

generate polymers exhibiting glassy (TPB-5), noncrystallizable nematic (TPB-4, TPB-6 to TPB-10), crystallizable nematic (TPB-11 to TPB-15), monotropic nematic (TPB-16 and TPB-17) and virtual nematic (TPB-18 to TPB-20) mesophases. This behavior is self-explanatory if we follow the plots from Figure 17. For example, some polymers are noncrystallizable since their glass transition temperature prohibits for kinetic reasons their crystallization. TPB-5 is only glassy since its glass transition temperature does not allow the formation of the mesophase, again for kinetic reasons. When the melting temperature is higher than the glass transition, these polymers can crystallize, while when melting is higher than isotropization they exhibit a virtual nematic mesophase only.

TPB-10 was synthesized with a perdeuterated spacer and the conformational and orientational order in the nematic phase was determined by D-NMR measurements and conformational calculations (Hardouin et al, 1995; Sherwood et al, 1994). Since this polymer does not undergo redistribution reactions as the polyesters do, its behavior is as predicted by theory (Yoon and Flory, 1989; Hardouin, 1995). Beginning at the isotropic-nematic transition at 104 °C, the polymer chains in the nematic phase adopt nearly fully extended (alternate trans) conformations and a rather high degree of orientational order parameter of ca. 0.85 is attained. As the temperature is lowered to 96 °C, the isotropic peak disappears completely, indicating the absence of any isotropic phase and hairpin conformations. With increasing supercooling, the conformational order shows little change, but the orientational order parameter increases continuously to ca. 0.95 at 80 °C. These results are therefore, in good agreement with the predictions of a recent theory on the nematic phase of a polymer comprising rigid and flexible

sequences in alternating succession (Yoon and Flory, 1989). When the 1,2-butane group from TPB is replaced by 1,2-propane, the new mesogen 1-(4-hydroxy-4'-biphenyl)-2-(4-hydroxyphenyl)propane (TPP) has a more cylindrical shape. This new mesogen, therefore resembles RBPE with $R = H$. The polyethers TPP-X with x containing an even number of methylenic units display highly ordered smectic phases while those with an odd number of methylenic units exhibit nematic mesophases (Percec et al, 1994 D). A detailed discussion on the molecular engineering of main chain liquid crystalline polyethers exhibiting nematic, smectic and columnar hexagonal mesophases as well as of their structure is available (Ungar, 1995).

8.9. HYPERBRANCHED AND DENDRIMERIC LIQUID CRYSTALLINE POLYMERS

Hyperbranched and dendrimeric macromolecules are a novel class of branched polymers which contain a branching point in each structural unit. Review articles on this topic are available (Hawker et al, 1994; Isberger et al, 1994; Tomalia et al, 1990; Tomalia and Durst, 1993; Tomalia, 1994). Hyperbranched polymers are obtained via step polymerization reactions of AB_2 monomers and therefore, exhibit a broad molecular weight distribution. Dendrimers are prepared by using a protection deprotection methodology in a divergent or convergent approach. This strategy yields monodisperse dendrimers.

The first examples of thermotropic hyperbranched polymers with disc-like mesogens (Percec et al, 1992 I) and rod-like flexible mesogens based on conformational isomerism (Percec and Kawasumi, 1992 L; Percec et al, 1994 G)

were reported from our laboratory. The synthesis of hyperbranched polyethers containing cyclotetrameratrylene units in the branching points was accomplished by the electrophilic polymerization of a 3,4-bis(n-alkyloxy)benzyl alcohol with an α,ω -bis{[2-(alkoxy)-5-(hydroxymethyl)phenyl]oxy}alkane (Scheme 31) (Percec et al, 1992 I). Scheme 32 outlines the preparation of TPD-b hyperbranched polymers, while their phase behavior is summarized in Table 14 (Percec and Kawasumi, 1992 L).

As observed from the results presented in Table 14, the phase behavior of these hyperbranched liquid crystalline polymers is strongly dependent on the nature of their chain ends (Percec and Kawasumi, 1992 L). Much broader thermotropic mesophases were obtained by using the synthetic procedure from Scheme 33. Of particular interest are the hyperbranched polymers TPT-b-8 since they display a very broad nematic mesophase (Table 15). Schemes 34-36 present the molecular design of four generations of monodisperse dendrons. The structure of the dendrimer based on these dendrons of the fourth generation is outlined in Scheme 37 (Percec, 1995 B; Percec and Chu, 1995 C). The phase behavior of these dendrons is outlined in Table 16. An entire new field of liquid crystalline polymers is emerging from hyperbranched and dendrimeric structures. Cholesteric hyperbranched liquid crystals were prepared by attaching chiral tails to hyperbranched nematic polymers (Bauer et al, 1993).

Independent and simultaneous with our work, an aromatic polyamide lyotropic dendrimer was obtained by the polycondensation of 5-amino-isophthaloyl chloride. However, the dendrimer obtained from the polymerization of 3,5-diaminobenzoyl chloride displays only a lyotropic phase (Kim, 1992 A; 1992 B).

8.10 CYCLIC MAIN CHAIN LIQUID CRYSTALLINE OLIGO- AND POLYETHERS

The membranes of archaebacteria, i.e., extremophile microorganisms which proliferate in extreme environments such as high temperature, acid, alkali or high salt concentration, are formed from macrocyclic oligoether lipids since these lipids are more stable than the corresponding linear ones (Yamauchi and Kinoshita, 1993). In 1992 it has been demonstrated that macrocyclic lipids display a thermotropic mesophase (Menger et al, 1992; 1993) and recently that they generate highly stable liposomes (Ladika et al, 1994).

Independently, in 1992, we have predicted and demonstrated that certain sizes of low-molar mass macrocyclics which are homologues of main chain liquid crystalline polymers based on conformationally flexible rod-like mesogens should and do exhibit a higher ability to generate liquid crystalline phases than do their low-molar-mass linear and both their linear and cyclic high molecular mass compounds (Figure 18) (Percec et al, 1992 M). The trend from Figure 18 is due to the fact that macrocyclics of a certain size which contain at least a minimum extent of ring strain and a proper combination of spacer and mesogenic lengths based on which they can generate a liquid crystalline phase, should have a lower entropy and therefore, must display higher transition temperatures (Percec and Keller, 1990 E) than the corresponding high molar mass linear and cyclic compounds. Scheme 1 outlines the *anti* and *gauche* conformers of 1-(4-hydroxybiphenyl-4-yl)-2-(4-hydroxyphenyl)butane (TPB) and the macrocyclization of TPB with α,ω -dibromoalkanes by a high dilution phase transfer catalyzed polyetherification. Optimum reaction conditions yield either the regioirregular linear polymer TPB-

(l)X(8) or a mixture of up to five sizes of regioirregular macrocyclics TPB-(c)X(z) which can be separated (where: l stands for linear, X represents the number of methylenic units in the spacer, c stands for cyclic and z is the degree of oligomerization of the macrocyclic compound). Both the regioirregular TPB-(l)X and TPB-(c)X(z) with $X = 2$ to 20 and $z = 1$ to 5 were synthesized and their phase behavior was investigated. Questions like: what is the shorter spacer X and the minimum ring size z of TPB-(c)X(z) which displays a liquid crystalline phase? what is the lowest size of the macrocyclic which displays a liquid crystalline phase whose isotropization temperature is higher than that of its linear high molar mass homologue (Percec et al, 1992 M; Percec and Kawasumi, 1993 I; 1994 J)? what is the probability of transforming kinetically prohibited (Percec and Kawasumi, 1992 B; 1993 A; 1993 I; 1993 J; 1994 J) and/or kinetically controlled (Percec and Kawasumi, 1993 J) mesophases of the linear polymer into enantiotropic mesophases via cyclization? what is the ability to generate noncrystallizable macrocyclics with a high glass transition temperature and a broad range of temperature of the mesophase (Percec and Kawasumi, 1993 A)? what is the dependence of the phase transition temperatures of a certain macrocyclic on its spacer length X and how does it compare with that of the corresponding linear polymer (Percec and Kawasumi, 1993 I)? were addressed, answered and explained.

Figure 19 outlines the synthesis of macrocyclic and linear polyethers based on TPB and α,ω -dibromoalkanes. The structure of these macrocyclics was confirmed by a combination of 300 MHz 1-D and 2-D ^1H -NMR experiments and by molecular weight determination (Percec et al, 1992 M).⁵²⁵ ^1H -NMR

spectroscopy was used to demonstrate that ring strain is released above the size of pentamer. The phase behavior of individual regioirregular linear monomer, dimer, trimer, tetramer TPB-(l)10 (Figure 20) and that of the high molecular weight linear polymers with narrow molecular weight distribution TPB-(l)10 is compared to that of the TPB-c(10) z ($z = 1$ to 5) in Figure 21 (Percec and Kawasumi, 1993 K).⁵²⁹ Both the linear and cyclic compounds from Figure 21 exhibit a nematic mesophase. The linear dimer has a higher isotropization temperature than the cyclic one. However, the cyclic trimer displays a much higher ability to form a nematic mesophase than the corresponding linear trimer. At the same time, the cyclic tetramer and pentamer exhibit much higher abilities to form nematic mesophases than even the very high molecular weight linear polymer. *These results demonstrate that at least in the case of the macrocyclic compounds based on TPB and 1,10-dibromodecane, the tetramer and pentamer and not the linear high molar mass polymers exhibit the highest tendency to form nematic mesophases.*

Figure 22a compares the isotropization temperatures (T_{ni}) of TPB-(c)10(4) and of TPB-(l)10 as a function of the number of methylenic units in the spacer. All TPB-(c)10(4) have higher T_{ni} values than the corresponding linear polymers. The ΔH_{ni} values of T_{ni} are plotted in Figure 22b. ΔH_{ni} of cyclics are lower than of the corresponding linear polymers since the difference between the entropies of a macrocyclic in isotropic and nematic phases is lower than the corresponding parameter of the linear polymer. The odd-even dependencies of T_{ni} and ΔH_{ni} of cyclic tetramers and linear compounds are similar.

Figure 23a plots the thermal transitions of TPB-(c)10(3) and Figure 23b their ΔH_{ni} values. Both sets of data of TPB-(c)10(3) (Figure 23) are different from

those of TPB-(c)10(4) (Figure 22). T_{ni} values of cyclic trimers show a very weak odd-even dependence of spacer length. However, this dependence (Figure 23a) follows the reversed trend of the data from Figure 22a. T_{ni} of cyclic trimers are increasing with the increase in spacer length while the same data of cyclic tetramers are decreasing. The cyclic trimers show higher T_{ni} for odd spacer length while cyclic tetramers and linear polymers for even spacer length. Both the T_{ni} and ΔH_{ni} values from Figure 23 demonstrate that the rigidity of cyclic trimers increases with the increase in spacer length. Therefore, while cyclic tetramers resemble the behavior of linear polymers, cyclic trimers represent a completely different class of LC. Finally, cyclic trimers with very short and very long spacers exhibit, in addition to the nematic mesophase, a smectic A (S_A) phase (Figure 23a). Regardless of the spacer length, the layer of the S_A phase of the cyclic trimers is equal to $1.5 \times (L_m + L_s)$ in which L_m is the length of the *anti* conformer of TPB while L_s is equal to the length of the flexible spacer in its fully extended all *trans* conformation (Figure 24). A trimer conformation like the middle right side of Figure 24 requires that $2L_m + L_s = 2 \times (L_s - 2.5) + L_m$ where 2.5\AA is the minimum length of the 180° turn in fold which is generated by two carbon atoms. Under these requirements the shorter spacer length (L_s) which can accommodate such a structure is equal or longer than L_m , i.e., $L_s \geq L_m$. At shorter spacer lengths a S_A phase can be found only when one TPB is in its *gauche* conformation and it is part of the fold (middle left trimer in Figure 24) (Percec and Kawasumi, 1993 B). Some experiments with macrocyclics based on enantiomerically enriched TPB suggest that intracyclic heterochiral recognition may have a contribution to the architecture of the larger macrocyclics in the nematic phase (Percec and Kawasumi,

1993 L) and that a superhelical shape is not excluded. In addition, the nematic phase of TPB-(c)9(3) seems to be biaxial (Li et al, 1993; 1994).

All these results suggest that in their liquid crystalline phase these compounds are *supramolecular rigid-rods generated from collapsed macrocyclics* (Figure 25). This novel class of liquid crystals has recently received interest in other laboratories (Ashton et al, 1994) and opens numerous avenues for the design of new macromolecular and supramolecular architectures based on liquid crystalline macrocyclic building blocks.

8.11 SIDE CHAIN LIQUID CRYSTALLINE POLYMERS

8.11.1 General Considerations

The field of side chain liquid crystalline polymers was recently reviewed (McArdle, 1989). Therefore, we will discuss only recent progress made on the molecular engineering of side chain liquid crystalline polymers. Most of the present discussion will be made on side chain liquid crystalline polymers with mesogenic groups normally attached to the polymeric backbone (Percec and Pugh, 1989 A). Figure 26 outlines the concept of side chain liquid crystalline polymers. It has been theoretically predicted (Warner, 1989; 1993) that the conformation of the polymer backbone should get distorted in the liquid crystalline phase. Both small-angle neutron scattering (SANS) experiments (Davidson et al, 1991; Hardouin et al, 1991; Noël, 1988; 1989; Noirez et al, 1988; 1995; Pepy et al, 1988) and X-ray scattering experiments (Davidson and Levelut, 1992; Kuschel et al, 1990; Mattoussi et al, 1986; Percec et al, 1990 C) have shown that the statistical random-coil

conformation of the polymer backbone is slightly distorted in the nematic phase and highly distorted in the smectic phase.

Let us now consider very briefly the influence of various parameters (i.e., nature of flexible spacer and its length, nature and flexibility of the polymer backbone and its degree of polymerization) on the phase behavior of a side chain liquid crystalline polymer. According to the thermodynamic schemes from chapter 8.5, the increase of the degree of polymerization decreases the entropy of the system and therefore if the monomeric structural unit exhibits a virtual or monotropic mesophase, the resulting polymer should most probably exhibit a monotropic or enantiotropic mesophase. Alternatively, if the monomeric structural unit displays an enantiotropic mesophase, the polymer should display an enantiotropic mesophase over a broader range of temperature. It is also possible that the structural unit of the polymer exhibits more than one virtual mesophase and therefore, at high molecular weights the polymer will increase the number of its mesophases. All these effects were observed with various systems (Percec and Pugh, 1989 A; Percec and Tomazos, 1992 A).

The length of the flexible spacer determines the nature of the mesophase. Long spacers favor smectic phases while short spacers favor nematic phases (Craig and Imrie, 1994; 1995; Percec and Tomazos, 1992 A). This effect is similar to that observed in low molar mass liquid crystals.

At constant molecular weight the rigidity of the polymer backbone determines the thermodynamic stability of the mesophase. According to the thermodynamic schemes described in chapter 8.5 the isotropization temperature of the polymer with more rigid backbone should be higher. However, experimentally

this situation is reversed. The highest isotropization transition temperature is observed for polymers with more flexible backbones. This conclusion is based on systematic investigations performed with two mesogenic groups which are constitutional isomers i.e., 4-methoxy-4'-hydroxy- α -methylstilbene (4-MHMS) (Percec and Tomazos, 1989 B) and 4-hydroxy-4'-methoxy- α -methylstilbene (4'-MHMS) (Percec and Tomazos, 1989 H) and polymethacrylate, polyacrylate, polysiloxane and polyphosphazene backbones (Percec and Tomazos, 1989 B; 1989 H; Percec et al, 1989 M) (Scheme 38). Recently a large number of data for the literature on side chain liquid crystalline polymers with different backbones and 4-cyanobiphenyl based mesogens were compiled and supported the same trend (Craig and Imrie, 1995). This dependence can be explained by assuming that a more flexible backbone uses less energy to get distorted and therefore generates a more decoupled polymer system. In fact the more flexible backbones do not generate only higher isotropization temperatures but also a higher ability towards crystallization. However, contrary to all expectations the entropy change of isotropization is higher for those polymers which are based on more rigid backbones and therefore, exhibit lower isotropization temperatures (Figure 27a,b) (Percec and Tomazos, 1990 I). This contradiction between the values of the entropy change and the isotropization temperatures can be accounted for by a different mechanism of distortion of different polymer backbones as outlined in Figure 28, that is, while a rigid backbone gets more extended and therefore, in the smectic phase it can cross the smectic layer, in the case of a flexible backbone it gets squeezed between the smectic layers. The higher configurational entropy of the flexible backbone versus that of the rigid backbone in the smectic phase can account

for the difference between the entropy change of isotropization from Figure 27. At shorter spacer lengths, there is not much difference between the contribution of various backbone flexibilities since most probably, in order to generate a mesophase they should get extended. Therefore, the entropy change of isotropization is less dependent of backbone flexibility (Figure 27).

Based on this discussion it is quite obvious that copolymers containing structural units with and without mesogenic groups and flexible backbone display a microphase separated morphology in their smectic phase (Figure 29) (Kuschel et al, 1990; Percec and Pugh, 1989 A; Percec et al, 1990 C). Therefore, the highest degree of decoupling is expected for copolymers containing mesogenic and nonmesogenic structural units and highly flexible backbones, i.e., microphase separated systems. In this last case, when the monomeric structural unit of the polymer exhibits a virtual mesophase, the high molecular weight polymer might also display only a virtual or a monotropic mesophase. The transformation of a virtual and/or monotropic mesophase of the homopolymers into an enantiotropic mesophase can be most conveniently accomplished by making copolymers based on two monomers which are constitutional isomers such as monomers based on 4-MHMS and 4'-MHMS (Percec and Tomazos, 1989 E; 1989 P). Since the structural units of the homopolymers based on 4-MHMS and 4'-MHMS are isomorphic within their liquid crystalline phase, but not within their crystalline phase, the crystalline melting transition decreases while the mesophase exhibits a continuous almost linear dependence on composition. As a consequence, the virtual or monotropic mesophase of the homopolymer becomes enantiotropic (Percec and Tomazos, 1989 E; 1989 P). Finally, the molecular weight at which the

isotropization temperature becomes independent of molecular weight should be, and indeed is, dependent on the flexibility of the polymer backbone. For example, the isotropization temperature of polysiloxanes (Gray, 1989; Richards et al, 1990) containing mesogenic side groups is molecular weight dependent up to much higher molecular weights than polymethacrylates containing mesogenic side groups (Percec and Pugh, 1989 A).

Based on this discussion and on the thermodynamic discussion from chapter 8.5, we can easily consider that the "polymer effect" can provide via its molecular weight and backbone flexibility the same effect. In an oversimplified way it can be considered that it provides an overall change in the entropy of the system. Through this change, it can transform, in a reversible way, a virtual mesophase into a monotropic and into an enantiotropic one. In addition, the kinetic factors provided by the glass transition and crystallization should always be considered. For example, the formation of a mesophase located in the close proximity of a glass transition temperature becomes kinetically controlled or even can be kinetically prohibited.

8.11.2 Molecular Engineering of Liquid Crystalline Polymers by Living Polymerization

8.11.2.1 General Considerations

Several polymerization methods were investigated in order to develop living polymerization procedures for the preparation of side chain liquid crystalline polymers with well defined molecular weight and narrow molecular weight

distribution. They include cationic polymerization of mesogenic vinyl ethers (Percec and Tomazos, 1987 C; Rodriguez-Parada and Percec, 1986), cationic ring opening polymerization of mesogenic cyclic imino ethers (Rodriguez-Parada and Percec, 1987), group transfer polymerization of mesogenic methacrylates (Kreuder et al, 1986; Percec et al, 1989 J; Pugh and Percec, 1985), polymerization of methacrylates with methylaluminium porphyrin catalysts (Kodaira and Mori, 1990) and metathesis polymerization of norbornenes containing mesogenic groups (Komiya et al, 1992 A; 1992 B; Komiya and Schrock, 1993 A; 1993 B; Pugh and Schrock, 1992; Pugh et al, 1994). Cationic polymerization has been proved to be the most successful since the initiators are very simple and it can be used to polymerize under living conditions mesogenic vinyl ethers containing a large variety of functional groups (Heroguez et al, 1990; Jonsson et al, 1991 A; 1991; Kostromin et al, 1990 A; Papon et al, 1992; Percec et al, 1991 E; 1992 R; Percec, 1991 B; 1991 F; 1991 P; Percec and Lee, 1991 A; 1991 G; 1991 H; Percec and Jonsson, 1993 F; Rodenhouse et al, 1990; Rodenhouse and Percec, 1991 A; 1991 C; Sagane and Lenz, 1988; 1989 A; 1989 B).

Scheme 39 provides some representative examples of mesogenic vinyl ethers which could be polymerized by a living mechanism by our preferred initiating system (i.e., $\text{CF}_3\text{SO}_3\text{H}$, $(\text{CH}_3)_2\text{S}$, CH_2Cl_2 , 0°C) (Cho et al, 1990). As we can observe from Scheme 39, vinyl ethers containing nucleophilic groups such as methoxybiphenyl (Jonsson et al, 1991 A), electron-withdrawing groups such as cyanobiphenyl (Jonsson et al, 1991 A; Percec et al, 1991 E; 1991 F; 1991 P; 1992 R; Percec and Lee, 1991 A; 1991 G; 1991 H), nitrobiphenyl and cyanophenylbenzoate (Jonsson et al, 1991 A), double bonds like in 4-alkoxy- α -

methylstilbene (Percec et al, 1991 P), double bonds and cyano groups like in 4-cyano-4'- α -cyanostilbene (Percec et al, 1991 F), aliphatic aromatic esters (Percec et al, 1991 B), acidic protons and perfluorinated groups (Percec et al, 1991 B; Jonsson et al, 1991 A), oligooxyethylene and aromatic ester groups (Rodenhouse and Percec, 1991 A), crown ethers and triple bonds (Percec and Johansson, 1993 F; Rodenhouse and Percec, 1991 C), all can be polymerized by a living cationic mechanism. In addition, cationic polymerization of any of these monomers can be performed in melt phase either in liquid crystalline or in isotropic phase by using thermal (Jonsson et al, 1991 C), or photo cationic initiators (Jonsson et al, 1991 B; 1992). When the polymerization is performed in liquid crystalline phase with aligned films of liquid crystalline monomers, perfectly aligned single crystal liquid crystalline polymer films are obtained (Jonsson et al, 1991 B; 1992).

In the following two subchapters we will discuss two topics. The first one refers to the influence of molecular weight on the phase transitions of poly{ ω -[(4-cyano-4'-biphenyl)oxy]alkyl vinyl ether}s with alkyl groups containing from four to eleven methylene units. In the second one we will demonstrate the molecular engineering of phase transitions of side chain liquid crystalline polymers by azeotropic living copolymerization experiments.

8.11.2.2 Influence of Molecular Weight on Phase Transitions of Poly{ ω -[(4-cyano-4'-biphenyl)oxy]alkyl vinyl ether}s

Scheme 40 outlines the general method used for the synthesis of ω -[(4-cyano-4'-biphenyl)oxy]alkyl vinyl ethers (6-n) and of the model compound for the polymer with degree of polymerization of one i.e., ω -[(4-cyano-4'-

biphenyl)oxy]alkyl ethyl ethers (8-n). We will use over the entire discussion the same short notations as in the original publications. The synthesis and characterization of poly(6-n) and (8-n) with $n = 2, 3, 4$ (Percec and Lee, 1991 A), 5, 7 (Percec and Lee, 1992 R), 6, 8 (Jonsson et al, 1991 A), 9, 10 (Percec and Lee, 1991 H), and 11 (Percec and Lee, 1991 E) will be briefly discussed. Details are available in the original publications. All polymers have polydispersities of about 1.10. Scheme 41 outlines the polymerization mechanism and the structure of the resulted polymers which was confirmed by 300 MHz 1-D and 2-D $^1\text{H-NMR}$ spectroscopy (Percec et al, 1992 G).

All data were classified according to their similarities. Figure 30 presents the dependence of phase transition temperatures of poly(6-n) with $n = 3, 4, 7$ and 9 as a function of molecular weight. These data were collected from second heating scans. The data for 8-n are not plotted. 8-3 is crystalline, 8-4 and 8-7 exhibit a monotropic nematic mesophase while 8-9 monotropic nematic and smectic mesophases. As we can observe from Figure 30 by increasing the molecular weight all four polymers show a broadening of the thermal stability of their mesophase. The mesophase of 8-7 and 8-9 changes from nematic to s_A by increasing the degree of polymerization from one to about 3.

Figure 31 presents similar data for poly(6-2), poly(6-6) and poly(6-8). In all cases the nature of the mesophase is molecular weight dependent. Poly(6-2) has a nematic mesophase only at degrees of polymerization lower than 5. 8-2 is only crystalline. At degrees of polymerization higher than 5 poly(6-2) is only glassy. This is because its glass transition temperature becomes higher than the isotropization temperature and therefore, the mesophase is kinetically prohibited. 8-

6 exhibits an enantiotropic nematic mesophase. At low degrees of polymerization poly(6-6) and poly(6-8) exhibit nematic and s_A mesophases. Due to the difference between the slope of the dependences of the nematic phase transition temperature on molecular weight and of the s_A phase transition temperature on molecular weight, above a certain molecular weight the nematic phase disappears. Both poly(6-6) and poly(6-8) show a second smectic mesophase (s_X , i.e. unassigned). Qualitatively, this behavior is in agreement with the influence of molecular weight on phase transitions predicted by thermodynamics (chapter 8.5). Quantitative predictions of these phase diagrams require more theoretical research.

Finally, Figure 32 presents the behavior of poly(6-5), poly(6-10) and poly(6-11). 8-5 shows an monotropic nematic phase, 8-10 a monotropic s_A phase while 8-11 an enantiotropic s_A mesophase. Poly(6-5) exhibits above a degree of polymerization of 10 the unusual sequence isotropic-nematic- s_{Ad} - n_{re} -glassy (Percec, 1992 C). This will be discussed in more detail in a subsequent subchapter. At high molecular weights poly(6-10) and poly(6-11) exhibit s_A and s_X phases.

As a general observation we can mention that polymers with short spacers ($n = 2, 3, 4$) and medium length spacers containing an odd number of methylene units ($n = 7, 9$) do not generate polymorphism at different molecular weights. Polymers with medium length and an even number of methylene units ($n = 6, 8$), as well as polymers with long length with both even and odd numbers of methylenic units ($n = 10, 11$) generate a rich polymorphism which is molecular weight dependent. The borderline polymer is poly(6-5) which is the only one displaying n

and s_A mesophases over a broad range of molecular weights and therefore also generates the reentrant nematic mesophase (Percec and Lee, 1992 C).

8.11.2.3 Molecular Engineering of Liquid Crystalline Phases by Living Cationic Copolymerization

In order to tailor make mesophases of side chain liquid crystalline copolymers we first need to synthesize copolymers with constant molecular weight and controllable composition. Copolymer composition is conversion dependent in all statistic copolymerizations. The only exception is provided by azeotropic copolymerizations in which the copolymer composition is identical to the monomer feed at any conversion (Tirrell, 1986). This situation is provided by monomers with $r_1 = r_2 = 1$. Since the reactivity of the polymerizable vinyl ether groups is not spacer length dependent, all 6-n monomers have the same reactivity. Therefore, all 6-n pairs of monomers lead to azeotropic copolymerizations, and when the copolymerization is performed under living conditions they lead to copolymers with controllable molecular weight. The azeotropic copolymerization of various pairs of 6-n monomers is outlined in Scheme 42. We will discuss selected examples of copolymers prepared from monomer pairs which give rise to homopolymers exhibiting nematic and nematic, s_A and s_A , nematic and s_A , and glassy and s_A phases as their highest temperature mesophases.

Figure 33 presents the dependence of phase transition temperatures obtained from second DSC heating scans (a,d), cooling scans (b, e) and the enthalpy changes associated with the highest temperature mesophase of copolymers poly[(6-3)-co-(6-5)]X/Y and poly[(6-6)-co-(6-11)]X/Y. The degrees of polymerization of

all copolymers are equal to 20 (Percec and Lee, 1991 J). Copolymers poly[(6-3)-co-(6-5)]X/Y are based on a monomer pair which gives rise to two homopolymers displaying an enantiotropic nematic mesophase as their highest temperature mesophase. As we can observe from Figure 33a,b,c the nematic-isotropic transition temperature and its associated enthalpy change show linear dependences of composition. This means that the structural units derived from poly(6-3) and poly(6-5) are isomorphic into their nematic mesophase. However, the same two structural units are isomorphic within the s_A mesophase exhibited by poly(6-5) only over a very narrow range of compositions. The linear dependence of the isotropization temperature is predictable by the Schroeder-Van Laar equations (Achard et al, 1989; Shroeder, 1893; Van Hecke, 1979; Van Laar, 1908). The same discussion is valid for the copolymer system poly[(6-6)-co-(6-11)]X/Y except that the isotropization temperature of these copolymers exhibit an upward curvature. This upward curvature is also predicted by the Schroeder-Van Laar equations (Achard et al, 1989; Shroeder, 1893; Van Hecke, 1979; Van Laar, 1908) and is due to the more dissimilar enthalpy changes associated with the isotropization temperatures of the two homopolymers.

Figure 34 presents the phase diagrams of copolymers poly[(6-3)-co-(6-11)]X/Y (Percec and Lee, 1991 J) and poly[(6-5)-co-(6-11)]X/Y (Percec and Lee, 1992 C). Both sets of copolymers have degrees of polymerization of 20. Both pairs of copolymers are based on monomers which give rise to homopolymers exhibiting nematic and s_A as their highest temperature mesophases. However, poly(6-5) displays a nematic and a s_A mesophase, while poly(6-3) only a nematic mesophase. Both sets of copolymers display continuous dependences of their

highest temperature mesophase with a triple point at a certain composition. This triple point generates over a very narrow range of compositions copolymers exhibiting the sequence isotropic-nematic- s_A - n_{re} . Again the shape of the dependences of the phase transition temperature on composition obeys the Schroeder-Van Laar equations.

Figure 35 presents two sets of phase diagrams obtained from monomer pairs giving rise to homopolymers which exhibit isotropic and s_A mesophases as their highest temperature mesophases, i.e., poly[(6-2)-co-(6-8)]X/Y with degree of polymerization of 10 (Percec and Lee, 1991 T; Percec et al, 1992 R), and poly[(6-2)-co-(6-11)]X/Y with degree of polymerization of 15 (Percec and Lee, 1991 N). Both sets of copolymers display a similar phase diagram. Over a certain range of compositions the two structural units are isomorphic within the s_A phase, after which follows a triple point. After this triple point the two structural units are isomorphic within a newly generated nematic mesophase. Both copolymers generate within a certain range of compositions on the left side of the triple point the sequence isotropic-nematic- s_A - n_{re} (Percec and Lee, 1992 C).³⁸⁴ Again the shape of the dependence of the highest temperature mesophase on composition is predictable by the Schroeder-Van Laar equations. This means that the structural units of all binary copolymers based on an identical mesogenic unit but different spacer lengths behave as an ideal solution. This behavior allows the engineering of mesomorphic phase transition temperatures and of their thermodynamic parameters in a straight forward manner by living azeotropic copolymerizations. The same behavior was demonstrated for monomer pairs which both give rise to homopolymers exhibiting a chiral smectic C mesophase (Percec et al, 1991 C).

Living homopolymerization and azeotropic copolymerization of monomer pairs which are diastereomers or enantiomers was used to investigate *hetero chiral* molecular recognition in pairs of monomer mixtures and polymer mixtures as well as in copolymers (Percec et al, 1994 F; Percec and Oda, 1994 H; 1994 I; 1995 A).

8.11.2.4 Side Chain Liquid Crystalline Polymers Exhibiting a Reentrant Nematic Mesophase

The reentrant nematic phase (n_{re}) was discovered in 1975 in low molar mass liquid crystals (Cladis et al, 1975). Since then it has received substantial theoretical and experimental interest (Cladis et al, 1977; Cladis, 1988; 1978; Goodby et al, 1984; Guillon et al, 1978; Hardouin et al, 1983; Hardouin, 1986; Sigaud et al, 1981; Tihn, 1983).

The first side chain liquid crystalline polymers exhibiting a n_{re} phase were reported in 1986 (Gubina, 1986; LeBarny, 1986). Some other examples of polymers exhibiting the sequence isotropic-nematic- s_{Ad} - n_{re} were reported in the meantime (Gubina et al, 1989; Kostromin et al, 1990 B; Legrand et al, 1990; Percec and Lee, 1992 C; Shibaev, 1988; Spassky et al, 1989). All these polymers are based on mesogenic units containing a cyano group, five or six atoms in the flexible spacer and a polyacrylate or polyvinyl ether backbone. The replacement of these quite flexible backbones with a more rigid one like polymethacrylate does not allow the formation of the n_{re} phase. As discussed in the previous subchapter a n_{re} mesophase can be generated by copolymerization of two monomers which lead to homopolymers with nematic or isotropic and s_A as their highest temperature mesophases, since these copolymers exhibit a triple point on their phase diagrams

(Percec and Lee, 1992 C). According to our experimental results any polymer which exhibits the sequence isotropic-nematic- s_A should also display a n_{re} phase. The most probable mechanism for the generation of a n_{re} phase is outlined in Figure 36 (Cladis, 1988). The most stable s_A phase of mesogens containing cyano groups is based on layers containing dimers of mesogens. On cooling, the nematic phase formed directly from the isotropic phase contains both dimeric mesogens and monomeric mesogens and so does the first s_A phase. In order to go from the less ordered s_A phase to the s_A phase based on dimeric mesogens, a n_{re} phase is required (Figure 36) (Cladis, 1988).

8.11.2.5 Influence of Tacticity on Phase Transitions

The tacticity of a polymer determines the flexibility and the conformation of its own backbone. Therefore, tacticity should affect the phase behavior of side chain liquid crystalline polymers at least in the same way as different polymer backbones with different flexibilities. Liquid crystalline polymethacrylates with atactic, syndiotactic and isotactic backbones were synthesized and characterized (Bohnert et al, 1993; Frosini et al, 1981; Hahn et al, 1981; Magagnini, 1981; Nakano et al, 1993; Okamoto et al, 1991). The general trend observed is that the most flexible backbones (i.e., those containing the lowest amount of syndiotactic sequences) give the highest isotropization temperatures. Polymers with higher syndiotactic sequences provide intermediary isotropization temperatures between atactic and isotactic ones. Isotactic polymers exhibit the lowest isotropization temperatures. This trend is also dependent on spacer length. Isotactic and

syndiotactic polymethacrylates have helical chain conformations while atactic have zig-zag (all-trans) conformations.

8.11.2.6 Cyclic Polysiloxanes Containing Mesogenic Side Groups

Low molecular weight (Hahn and Percec, 1988; Percec and Hahn, 1989 C) and high molecular weight (Richards et al, 1990) cyclic polysiloxanes containing mesogenic side groups were reported. Figure 37 presents the dependence of the isotropization temperature on the degree of polymerization for linear and cyclic polysiloxanes containing cyanophenyl benzoate groups connected to the backbone by a pentyl spacer (Richards et al, 1990). Isotropization temperatures of cyclic polymers are higher than those of the linear polymers. However, more research is required to reach the same level of understanding between structure and properties in this class of polymers as that available presently for cyclic, amorphous and crystalline polymers (Percec et al, 1989 L). A general review on various classes of liquid crystalline polysiloxanes is available (Boileau and Teyssié, 1991).

8.11.2.7 Side Chain Liquid Crystalline Polyacetylenes

Monosubstituted acetylenes (LeMoigne et al, 1989; 1991 A; 1991 B; Oh et al, 1993 A; 1993 B; Zhang et al, 1990) and p-substituted phenylacetylenes (LeMoigne et al, 1992) containing various mesogenic side groups were synthesized and polymerized by Ziegler-Natta and metathesis catalysts. Conjugated polyacetylenes exhibiting nematic, cholesteric and various smectic phases were reported. Additional research is required to establish the dependence between polymer molecular weight and double bonds configuration (i.e., cis-cisoidal, cis-

transoidal, trans-transoidal and trans-cisoidal) on phase transitions. All these polymers exhibit interesting nonlinear optical properties and electrical conductivity which are both anisotropic.

A very interesting class of liquid crystalline polyacetylenes is obtained by the metathesis cyclopolymerization of various dipropargyl derivatives containing mesogenic groups (Choi et al, 1994 A; 1994 B; 1994 C; Jin S.-H. et al, 1991; 1993). A fully conjugated poly(1,6-heptadiyne) backbone containing mesogenic side groups is obtained. Selected examples of monomers and the corresponding polymers are outlined in Scheme 43. Conducting side chain liquid crystalline polymers with nematic and various smectic phases were obtained by this synthetic procedure.

8.12 IONIC LIQUID CRYSTALLINE POLYMERS

Ionic liquid crystalline polymers are of recent research interest but of great potential from both synthetic as well as from their properties point of view. We will only mention very briefly a few selected examples from various research trends since structure-properties relationships in this field is far from being elaborated.

8.12.1 Main Chain Ionen Liquid Crystal Polymers

Quarternization of 4,4'-bipyridyl with α,ω -dibromoalkanes yield thermotropic oligomers bearing viologen mesogenic groups (Paleos et al, 1986; Yu and Samulski, 1994). Other examples of thermotropic ionenes we synthesized by a similar procedure from α,ω -dielectrophilic alkanes and trans-1,2-bis(4-pyridyl)ethene. The size of the counteranion derived from the electrophilic group of

the α,ω -dielectrophilic alkane has a strong influence on the thermotropic properties of the resulting polymer (Yousif et al, 1990). The salts obtained from α,ω -diaminoalkanes and α,ω -alkanedicarboxylates also form thermotropic mesophases (Sellens et al, 1989).

8.12.2 Side Chain Ionic Liquid Crystal Polymers

Alkylation of polyethyleneimine with an alkylhalide containing mesogenic groups yields thermotropic liquid crystalline polyethyleneimines with ammonium halide groups in the main chain. Smectic mesophases are easily obtained (Ujiie and Iimura, 1990; 1991 A; 1991 B; 1992). Alkylation or protonation of poly(4-vinylpyridine) and of other polymers containing 4-substituted pyridine side groups with ω -halides of mesogenic groups represents another method for the preparation of ionic side chain polymers (Brandys and Bazuin, 1993).

8.12.3 Liquid Crystalline Polyelectrolyte Complexes

The complexation of poly(acrylic acid) with dodecyltrimethylammoniumchloride and of poly(styrene sulfonate) (Antonietti and Conrad, 1994 A) with different alkyltrimethylammonium derivatives (Antonietti et al, 1994 B) by common precipitation in water yields liquid crystalline polyelectrolyte-surfactant complexes. These complexes represent a novel class of liquid crystalline materials with very large synthetic capabilities.

8.13 LIQUID CRYSTALLINITY INDUCED VIA INTER- AND INTRACHAIN ELECTRON-DONOR-ACCEPTOR (EDA) INTERACTIONS

Both intrachain and interchain electron donor-acceptor (EDA) interactions between repeat units containing one mesogenic group with electron donor and the other with electron acceptor character were used to enhance the phase behavior of copolymers and of polymer blends. The positive deviations of the isotropization temperature from the ideal ones were observed in the copolymers obtained from acceptor and donor mesogenic monomers (Imrie et al, 1991; Imrie and Paterson, 1994; Kosaka and Uryu, 1995; Schleeh et al, 1993). A mesophase was induced by blending two amorphous polymers containing mesogenic groups with donor and respectively acceptor mesogenic groups (Imrie and Paterson, 1994). A smectic phase was induced in a blend based on two homopolymers which each exhibit only a nematic mesophase (Kosaka and Uryu, 1994). The use of donor-acceptor interactions to manipulate the phase behavior and to induce new mesophases in mixtures of low molar mass liquid crystals is more extensively investigated and the transplant of this concept to the field of polymers is only at the beginning.

8.14 LIQUID CRYSTALLINE POLYMERS CONTAINING CROWN ETHERS AND POLYPODANTS

Mesomorphic host-guest systems of low molecular weight and polymer liquid crystals containing macroheterocyclic ligands and polypodants provide a novel approach to self-assembled systems which combine selective recognition with external regulation (Cram, 1988; Lehn, 1988; 1990; 1993; Pedersen, 1988). Three

basic architectures can be considered for liquid crystalline polymers containing crown ethers (Figure 38): main chain liquid crystalline polymers containing crown ethers in the main chain of the polymer and side chain liquid crystalline polymers containing crown ethers either in the mesogenic group or in the main chain. Alternatively, the same series of polymers with polypodants instead of crown ethers can be considered.

Main chain polyamides and polyethers containing crown ethers were reported (Cowie and Wu, 1988; Percec and Rodenhouse, 1989 G). A variety of side chain liquid crystalline polymers containing crown ether groups at one end of the mesogenic unit were designed (Hsiue et al, 1991; Percec and Rodenhouse, 1989 K; 1991 D; Percec et al, 1992 K; Percec and Johansson, 1993 F; Rodenhouse and Percec, 1991 B; 1991 C; Ungar et al, 1991 C; Wen et al, 1990). Side chain liquid crystalline polymers containing crown ethers in the main chain were synthesized by living cationic cyclopolymerization and cyclocopolymerization of 1,2-bis(2-ethenyloxyethoxy)benzene derivatives containing mesogenic side groups (Rodenhouse et al, 1990, Rodenhouse and Percec, 1991 A). Polymers containing crown ethers in the side groups dissolve ion-pairs and behave as copolymers containing two different mesogenic groups, i.e., complexed and uncomplexed. Their behavior is similar to that of copolymers derived from two different mesogenic groups. Therefore, their phase behavior is directed by molecular recognition (Percec et al, 1992 K, Percec and Johansson, 1993 F). The use of oligooxyethylenic spacers in main chain (Shaffer and Percec, 1987), and side chain (Hsieh et al, 1990 B; Percec and Tomazos, 1993 G; 1993 H; Rodriguez-Parada and Percec, 1986) liquid crystalline polymers leads to liquid crystalline polypodants.

Both main chain (Shaffer and Percec, 1987) and side chain (Percec and Tomazos, 1993 G; 1993 H) liquid crystalline polypodants dissolve large amounts of alkali metal salts, and the resulting liquid crystalline polyelectrolytes are ionic conductors (Hsieh et al, 1990 A). A detailed review on molecular, macromolecular and supramolecular liquid crystals containing macroheterocyclic ligands is available (Percec and Johansson, 1995). A general discussion on reactions and interactions in liquid crystalline media is also available (Percec et al, 1992 S).

8.15 ELECTRON DONOR-ACCEPTOR (EDA) COMPLEXES OF LIQUID CRYSTALLINE POLYMERS CONTAINING DISCOTIC MESOGENS

Ringsdorf et al. have studied the effect of doping with electron acceptor molecules on the phase behavior of polymers containing disc-like donor mesogens (Bengs et al, 1991; Eigen and DeMaeyer 1966, Eigen, 1971; Green et al, 1990, Paulus et al, 1991; Ringsdorf et al, 1989; Ringsdorf and Wustefeld, 1990). They demonstrated that charge transfer interactions increase the degree of order within the liquid crystalline phase, and also stabilize the liquid crystalline mesophase. For example, when a discotic main-chain polyester was doped with 2,4,7-trinitrofluorenone (TNF), the width of the discotic columnar hexagonal mesophase was increased by ~ 50 °C, for molar ratios of polymer/TNF equal to 3/1 and 2/1 (Scheme 44) (Ringsdorf et al, 1989). The intermolecular spacing decreased also considerably, proportional to the amount of TNF present in the complex. The same authors doped a non-liquid crystalline main-chain polyester containing disc-like mesogens and this resulted in the induction of a discotic columnar mesophase

(Scheme 44). The intercolumnar spacings found were extremely large and the authors assumed that considerable amount of TNF was uncomplexed and was located in the intercolumnar spacing. Further, doping of a non-liquid crystalline polymethacrylate containing donor disc-like groups in the side-chain resulted in the formation of a nematic columnar mesophase (Scheme 45). Doping also induced compatibility and liquid crystallinity in an incompatible mixture of non-mesogenic electron donor polymers, i.e. a polymethacrylate and a polyester. The resulting discotic polymer blend exhibited a nematic columnar phase (Scheme 46) (Ringsdorf et al, 1989). Finally, chirality was induced in a discotic liquid crystalline polymer by doping with a chiral acceptor (Green et al, 1990).

Research on liquid crystalline polymers containing disk-like mesogens was restricted by their difficult multi-step and low yield synthesis. Recently, a very convenient and universal procedure for the preparation of triphenylene-based discotic liquid crystalline polymers was reported (Boden, et al 1995). This development will allow detailed investigations of polymers containing discotic mesogens.

8.16 MOLECULAR RECOGNITION DIRECTED SELF-ASSEMBLY OF SUPRAMOLECULAR LIQUID CRYSTALLINE POLYMERS. H-BONDING AND OTHER INTERACTIONS

The molecular recognition of complementary components leads to systems able to self-assemble i.e., systems capable to generate spontaneously a well defined supramolecular architecture from their components under a well-defined set of conditions (Lehn, 1988; 1990).

Although self-assembly is a well recognized process in biological systems (Eigen and DeMaeyer, 1966; Eigen, 1971; Klug, 1983), the general concept of self-assembly of synthetic molecules by molecular recognition of complementary components, received a revived interest only after it was integrated by Lehn in the new field of supramolecular chemistry (Lehn, 1988; 1990; 1993; Lindsey, 1991; Philp and Stoddart, 1991; Vögtle, 1989; 1991; Weber, 1993; Whitesides et al, 1992).

Several examples in which molecular recognition induces the association of complementary nonmesomorphic components into a low molar mass or polymeric supramolecular liquid crystal are described below.

The principles of formation of a mesogenic supramolecule from two complementary components is outlined in Scheme 47. The particular example used by Lehn et al (Brienne et al, 1989) to generate a supramolecular disc-like mesogenic group which displays a hexagonal columnar mesophase is by formation of an array of three parallel hydrogen bonds between groups of uracil and 2,6-diaminopyridine type (Scheme 48).

The transplant of the same concept to the generation of a supramolecular liquid crystalline polymer is outlined in Scheme 48 (Fouquey et al, 1990). The complementary moieties TU_2 and TP_2 are uracil (U) and 2,6-diacylamino-pyridine (P) groups connected through tartaric acid esters (T). The tartaric acid (T) unit provides in addition, the opportunity to investigate the effect of chirality on the mesomorphic behavior of the species formed. Thus the components LP_2 , LU_2 , DP_2 , MP_2 and MU_2 are derived from L(+), D(-) and meso (M) tartaric acid respectively. Although all monomers (LP_2 , LU_2 , DP_2 , MP_2 and MU_2) are only

crystalline, the corresponding supramolecular "polymers" obtained through hydrogen bonding ($LP_2 + LU_2$, $DP_2 + LU_2$ and MP_2 and MU_2) exhibit hexagonal columnar mesophases. These hexagonal columnar mesophases are generated from helices which have a cylindrical suprastructure (Forquey et al, 1990).

An additional example of supramolecular liquid crystalline polymer obtained through the hydrogen bonding of nonmesomorphic monomers was recently reported (Fornaiser et al, 1990).

Examples in which a mesophase was generated through dimerization of carboxylic acid derivatives via hydrogen bonding were available in the classic literature on liquid crystals and were extensively reviewed (Eidenschink, 1989; Gray, 1962; 1974; 1979; 1982; 1985). New and interesting examples on the generation of nonsymmetrical liquid crystalline dimers (Kato and Fréchet, 1989 A), twin dimer (Kato et al, 1990 A; 1990 B), side chain liquid crystalline polymers (Kato and Fréchet, 1989 B; Kato et al, 1992; 1993; Kumar et al, 1992 A; 1992 B), main chain liquid crystalline polymers (Alexander et al, 1994; Bladon and Griffin, 1993; Lee, C.-M. et al, 1994) and supramolecular networks (Kato et al, 1994; Wilson, 1994 B) by specific hydrogen bonding "reactions" are under active investigation in several laboratories (Scheme 49).

Recently, a new approach to molecular recognition directed self-assembly of supramolecular structures displaying liquid crystallinity by a mechanism which resembles that of the self-assembly of tobacco mosaic virus (TMV) was reported (Johansson et al, 1994; Kwon et al, 1994 A; 1995; Percec et al, 1991 I; 1992 D; 1992 E; 1993 C; 1993 D; 1993 E; 1994 A; Tomazos et al, 1994; Ungar et al, 1994 A). The self-assembly mechanism of TMV is outlined in Figure 39 (Klug, 1983).

The synthetic approach can be summarized as follows. A flexible polymer backbone containing tapered side groups self-assembles the side groups into a column which surrounds the polymer backbone (Figure 40). These polymers exhibit thermotropic hexagonal columnar mesophases. Although the number of chains penetrating through the center of the column is not yet known and requires further research, it seems that this self-assembling system is complementary to those elaborated by Lehn et al. (Brienne et al, 1989; Forquey et al, 1990) In the model elaborated by Lehn et al. (Brienne et al, 1989; Forquey et al, 1990) the complementary pairs are self-organized through hydrogen bonding type interactions (endo-recognition), while in the last case (Johansson et al, 1994; Klug, 1983; Kwon et al, 1994 A; 1994 B; 1995; Percec et al, 1991 I; 1992 D; 1992 E; 1993 C; 1993 D; 1993 E; 1994 A; Tomazos et al, 1994; Ungar et al, 1994 A) the combination of taper-shaped side groups and the interactions generated by functional groups attached to them are responsible for the generation of a polymeric column. By analogy with the self-assembly of TMV this self-assembling process can be generated with and without a polymer backbone. Some reviews on this process are available (Percec et al, 1994 B; 1994 C; 1994 E; 1994 K).

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FIGURE CAPTIONS

Figure 1 Schematic representation of main chain, side chain, and combined liquid crystal polymers.

Figure 2 Schematic plot of free energies versus temperature for a system that does not show a mesophase. G_k , G_{lc} and G_i are, respectively, the free energies of the crystalline, mesomorphic (virtual) and isotropic liquid states. $T_{k-i} = T_m$ is the crystalline melting point. Here, as in subsequent Figures 3 to 6, the heaviest lines correspond to the stablest state at a given temperature.

Figure 3 Schematic plot of free energies versus temperature for the system in Figure 2 but with G_i raised (to G_i') so as to "uncover" the mesophase. T_{k-lc} and T_{lc-i} are the crystal-mesophase transition and the isotropization transition temperatures.

Figure 4 Schematic plot of free energies versus temperature for the system in Figure 2 but with G_k raised (to G_k') so as to "uncover" the mesophase.

Figure 5 Schematic plot of the free energy diagram illustrating the origin of a monotropic liquid crystal. Here, as in Figure 2, the arrows represent heating and cooling pathways.

Figure 6 Schematic free energy diagram for an enantiotropic liquid crystal, where the mesophase is metastable.

Figure 7 The broadening of the temperature range of an enantiotropic mesophase of the monomeric structural unit (M_0) by increasing the degree of polymerization. The upper part (a) describes the influence of molecular weight on the dependence between the free energies of the crystalline (G_k), liquid crystalline (G_{lc}) and isotropic (G_i) phases and transition temperatures. The translation of this dependence into the dependence phase transition temperature-molecular weight is presented in the lower part (b).

Figure 8 Transformation of a virtual or monotropic mesophase of the monomeric structural unit (M_0) into an enantiotropic mesophase by increasing the degree of polymerization. The upper part (a) describes the influence of molecular weight on the dependence between the free energies of the crystalline (G_k), liquid crystalline (G_{lc}) and isotropic (G_i) phases and transition temperatures. The translation of this dependence into the dependence phase transition temperature-molecular weight is presented in the lower part (b).

Figure 9 The narrowing of the temperature range of a virtual mesophase of the monomeric structural unit (M_0) by increasing the degree of polymerization. The upper part (a) describes the influence of molecular


weight on the dependence between the free energies of the crystalline (G_k), liquid crystalline (G_{lc}) and isotropic (G_i) phases and transition temperatures. The translation of this dependence into the dependence phase transition temperature-molecular weight is presented in the lower part (b).

Figure 10 The dependence of various first order transitions on molecular weight for a rigid rod-like polymer.

Figure 11 a) Definition of the axial ratio ($\alpha=L/d$) in the model of rigid rod-like mesogen and polymer; b) model for flexible and semi-rigid main chain liquid crystalline polymer (l defines the Kuhn's segment).

Figure 12 a) Board formation of highly substituted rigid rod polymers, caused by hindered rotation of their mesogenic units (Ringsdorf et al, 1987); b) schematic representation of a sanidic (from Greek for boardlike) mesophase (Schoenherr et al, 1986).

Figure 13. DSC curves of polyethers based on MBPE and 1,5-dibromopentane (MBPE-5), MBPE and 1,8-dibromooctane (MBPE-8) and corresponding copolyethers [MBPE-5/8(A/B)]. a): First (—) and second (- - -) heating scans; b): cooling scans.

Figure 14 a) Thermal transitions of polyethers (MBPE-5 and MBPE-8) and copolyethers [MBPE-5/8(A/B)]. First heating scan [(


b) Enthalpy changes of polyethers (MBPE-5 and MBPE-8) and copolyethers [MBPE-5/8(A/B)]. First heating scan [(

Figure 15 a) Dependence of the virtual isotropic-nematic (T_{in}) phase transition temperature of MBPE-X homopolymers on the number of methylene units in the flexible spacer (X). Upper right side corner presents the logarithmic plot of this dependence. b) Dependence of the virtual isotropic-nematic (T_{in}) phase transition temperature of MBPE-X homopolymers on the inverse of the number of methylene units in the flexible spacer ($1/X$). The logarithmic dependence is presented with a continuous line.

Figure 16 Schematic representation of columnar and smectic mesophases exhibited by polyethers and copolyethers based on BPE, PEB and 1,9-dibromononane.

Figure 17 Dependence of phase transition temperatures of TPB-X polyethers on the number of methylenic units in the flexible spacer (X): a) data from the second heating scan (T_g data of TPB-11 to TPB-20 are from the first heating scan); b) data from the first cooling scan.

Figure 18 The theoretical and experimental dependence of the isotropization temperature (T_i) of cyclic and linear main-chain liquid crystalline polymers on their degree of polymerization (DP). Both T_i and DP are in arbitrary units.

Figure 19 Conformational isomerism of TPB and its regioirregular cyclization with 1,10-dibromodecane under high-dilution conditions.

Figure 20 The structures of the linear regioirregular model compounds of TPB-(l)10.

Figure 21 Dependence of the isotropic-nematic (T_{in}) transition temperatures of regioirregular linear (\square) and macrocyclic (\circ) oligomers and polymers of TPB-(l)10 on their degree of polymerization.

Figure 22 The dependence of the isotropic-nematic transition temperature (T_{ni}) (a) and of its associated enthalpy changes (ΔH_{ni}) (b) of regioirregular TPB-(c)X(4) (cyclic tetramer) and TPB-(l)X (high molecular weight linear polymer) on spacer length (X).

- Figure 23 The dependence of the various transition temperatures (a) and of the enthalpy changes (b) associated with the nematic-isotropic (ΔH_{ni}) transition temperatures of regioirregular TPB-(c)X(3) (cyclic trimer) versus spacer length (X).
- Figure 24 The ideal architecture of cyclic oligomers (dimer to pentamer) in the crystalline and liquid crystalline phases.
- Figure 25 Schematic representation of the suggested mechanism for the isotropic-nematic transition of TPB-(c)X(4).
- Figure 26 Schematic representation of side chain liquid crystalline polymers showing the necessity of decoupling the mesogenic groups and the polymer backbone through flexible spacers.
- Figure 27 a) The dependence between the entropy change of isotropization (ΔS_i) determined from the cooling DSC scans, the nature of the polymer backbone and the number of methylenic units (n) in the flexible spacer for the series of polymers based on 4-MHMS isomer.
b) The dependence between the entropy change of isotropization (ΔS_i) determined from the cooling DSC scans, the nature of the polymer backbone and the number of methylenic units (n) in the flexible spacer for the series of polymers based on 4'-MHMS isomer.

Figure 28 a) Schematic representation of the theoretical distortion of the statistical random-coil conformation of the polymer backbone in the nematic and smectic phases; b) Two possible modes of distortion of the random-coil conformation of a rigid (left) and a flexible (right) polymer backbone. R_{\parallel} refers to the radius of gyration parallel to the magnetic field. The radius of gyration perpendicular to the magnetic field is labelled as R_{\perp}

Figure 29 Microphase separated morphology of smectic copolymers.

Figure 30 The influence of molecular weight on the phase behavior of poly(6-3), poly(6-4), poly(6-7) and poly(6-9) (determined from second DSC heating scans)

Figure 31 The influence of molecular weight on the phase behavior of poly(6-2), poly(6-6) and poly(6-8) (determined from second DSC heating scans)

Figure 32 The influence of molecular weight on the phase behavior of poly(6-5), poly(6-10) and poly(6-11) (determined from second DSC heating scans)

Figure 33 The dependence of phase transition temperatures obtained from second heating scan (a,d), cooling scan (b,e), and the enthalpy changes associated with their highest temperature mesophase of copolymers poly[(6-3)-co-(6-5)]X/Y and poly[(6-6)-co-(6-11)]X/Y (all with degrees of polymerization equal to 20)

Figure 34 The dependence of phase transition temperatures obtained from second heating scan (a,d), cooling scan (b,e), and the enthalpy changes associated with their highest temperature mesophase of copolymers poly[(6-3)-co-(6-11)]X/Y and poly[(6-5)-co-(6-11)]X/Y (all with degrees of polymerization equal to 20)

Figure 35 The dependence of phase transition temperatures obtained from second DSC heating scan (a,d), cooling scan (b,e), and the enthalpy changes associated with their highest temperature mesophase of copolymers poly[(6-2)-co-(6-8)]X/Y and poly[(6-2)-co-(6-11)]X/Y (with degrees of polymerization equal to 10 and 15, respectively)

Figure 36 The mechanism of formation of the re-entrant nematic mesophase (Cladis, 1975).

Figure 37 Isotropization transition temperatures of cyclic (●) and linear (□) polysiloxanes containing cyanophenyl benzoate mesogen connected to the backbone via a pentyloxy group (Richards et al, 1990).

Figure 38 The molecular architecture of liquid crystalline polymers containing crown ether ligands.

Figure 39 Self-assembly of tobacco mosaic virus (TMV). The protein subunits define the shape of the helix and the RNA defines the helix length. All

information for assembly is contained within the component parts. The structure contains $16\frac{1}{3}$ protein subunits per turn and 2130 identical protein subunits (17,500 daltons each). The virus dimensions are 3000 Å in length, 180 Å in diameter, a helical pitch of 23 Å, a central hole of 40 Å, with 3 nucleotides bound per protein subunit (Percec et al, 1994 C).

Figure 40 The self-organization of a randomly coiled flexible polymer containing tapered side groups into a rigid rod-like columnar structure.

Table 1. Melting and Isotropization Transitions of Poly(p-phenylene)s

n	axial ratio $x = L/d$	T_{n-i} (°C) Estimated ^a	Polymorphism
2	≈ 2	---	$T_{k-i} = 70$ °C
3	≈ 3	---	$T_{k-i} = 210$ °C
4	≈ 4	≈ 120	$T_{k-i} = 320$ °C
5	≈ 5	≈ 450	$T_{n-i} = 430$ °C
6	≈ 6	≈ 1900	$T_{n-i} = 560$ °C
7	≈ 7	not isotropic	$T_{k-n} \approx 550$ °C (also decomposition)

^a The estimated T_{n-i} has been normalized on quinquephenyl ($n = 5$).

Table 2. Molecular structures of aromatic polyamides

Head-to-head phenyl and biphenyl polyamides

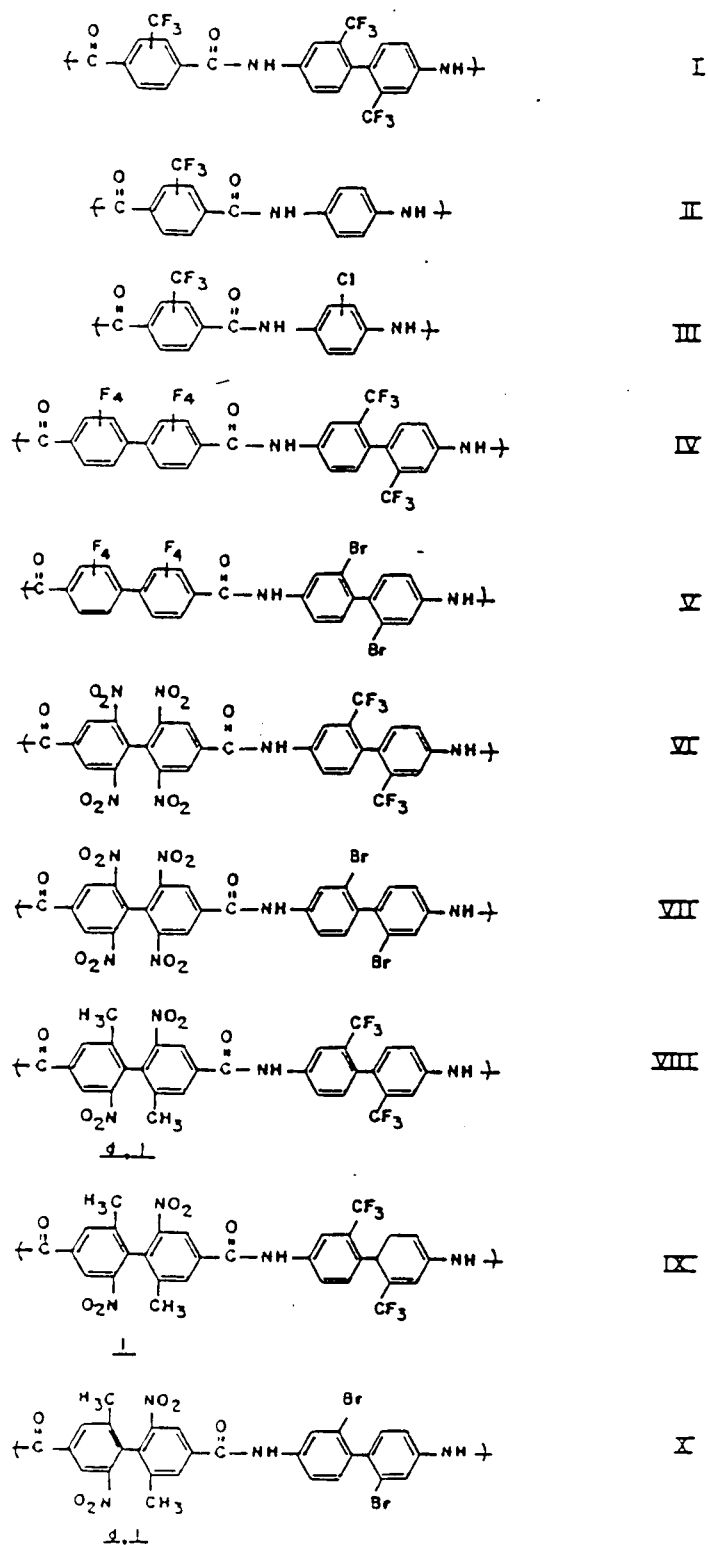
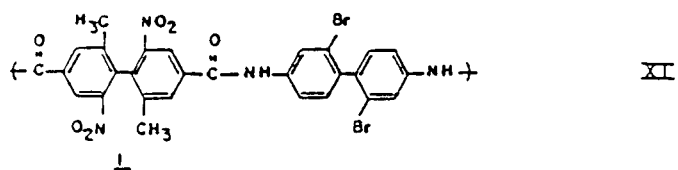
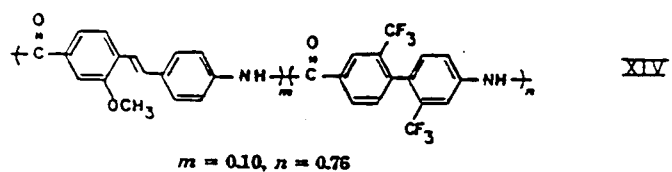
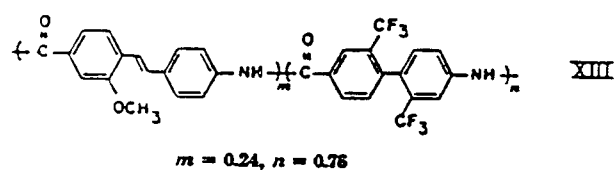
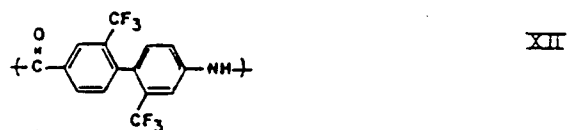


Table 2. (Continued)



Head-to-tail biphenyl polyamides



Substituted terphenyl and quaterphenyl polyamides

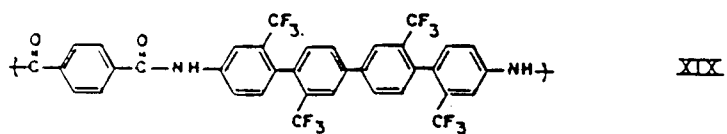
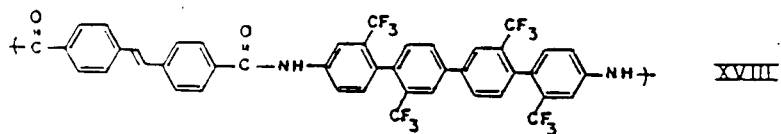
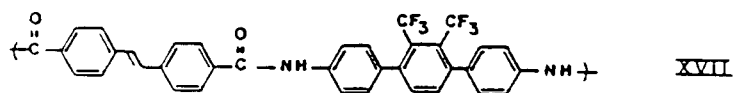
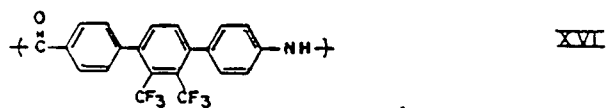
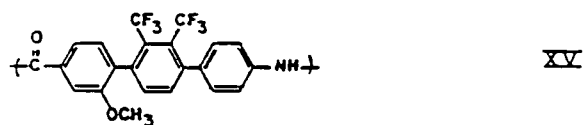


Table 3. Viscosity and Solubility Properties of Biphenyl Polyamides

Polymer	$\eta_{inh}(dl/g)^a$	Solubility			
		LiCl/ Amides ^b	Amides	Ethers ^c	Ketones ^d
I	3.23	S ^e	44-48 ^f	Sw	Ins
II	1.84 (DMAc)	S	S	Ins	Ins
III	2.34 (DMAc)	S	S	Ins	Ins
IV	1.19	S	Sls	Ins	Ins
V	1.68	S	Ins	Ins	Ins
VI	1.27	S	S	S ^g	Ins
VII	1.10	S	S	Ins	S
VIII	1.75	S	S	36 (THF)	S
IX	0.91	S	S	25 (THF)	S
X	2.46	S	S	17 (THF)	Ins
XI	1.68	S	S	14 (THF)	Ins
XII	5.0	S	S	S	S
XIII	4.74	S	S	Ins	Ins
XIV	4.94	S	S	S	S
XV	1.39	S	S	Ins	Ins
XVI	---	Ins	Ins	Ins	Ins
XVII	2.30	S	Ins	Ins	Ins
XVIII	1.31	S	S	S	S
XIX	6.04	S	S	Sls	S

^a 0.5% polymer (w/v) / 5% (w/v) LiCl/DMAc at 30 °C^b Amide solvents: DMAc, TMU, and NMP^c Ether solvents: THF, glymes, but not diethyl ether, dioxane^d Ketone solvents: acetone and cyclohexanone^e S, soluble; Sw, swells; Sls, slightly soluble; Ins, insoluble^f w/v%^g Methoxy ethanol but not THF

Table 4. Phenyl-substituted aromatic polyamides^a

	Inherent viscosity η_{inh} , ^b dL/g			Solubility in DMAc or NMP, g/100g ^d
	H ₂ SO ₄ ^c	DMAc ^d		
<chem>*C(=O)c1ccc(cc1)-c2ccccc2C(=O)Nc3ccc(cc3)N*</chem>	0.61	1.10		50
<chem>*C(=O)c1ccc(cc1)-c2ccccc2C(=O)Nc3ccc(cc3)Nc4ccc(cc4)C(=O)Nc5ccc(cc5)C(=O)c6ccccc6C(=O)N*</chem>	3.28	7.55		18
<chem>*Nc1ccc(cc1)C(=O)Nc2ccc(cc2)C(=O)c3ccccc3C(=O)Nc4ccc(cc4)C(=O)N*</chem>	1.45	2.52		20
<chem>*C(=O)c1ccc(cc1)-c2ccccc2C(=O)Nc3ccc(cc3)Nc4ccc(cc4)C(=O)Nc5ccc(cc5)C(=O)c6ccccc6C(=O)N*</chem>	2.28	3.32		14-15

^a All polymers prepared by the phosphorylation method

^b 0.5% concentration at 25 °C

^c 96% H₂SO₄

^d Containing 4% LiCl

Table 5. Characterization of polymers from bicyclo[2.2.2]octane-1,4-dicarboxylic acid and 2,5-dialkoxyhydroquinone diacetates (PBCOHQ-n)

n ^a	[η] ^b	layer spacing d, Å	Thermal transitions ^c			
			Heating		Cooling	
			T _s	T _m	T _s	T _m
6	1.10	10.1	63 ^d	315		254
8	0.99	11.5	60 ^d	255		210
10	1.21	12.8	55 ^d	243		204
12	0.53	15.2	28	223	-2	186
14	0.87	16.5	46	206	30	166
16	0.59	17.8	60	193	49	160

^a Number of carbon atoms in the side chain

^b In dL/g, measured in CH₂Cl₂/TFA (95/5 (v/v)) at 20 °C

^c In °C. Heating and cooling rates: 20 °C/min

^d Transition observed only in the first heating scan

Table 6. Characterization of polymers from terephthalic acid and 2,5-dialkoxyhydroquinones (PTAHQ-n)

n ^a	Thermal transitions ^e									
	layer spacing			Heating			Cooling			
	[η] ^b	d, Å ^c	d, Å ^d	T _s	T _m	T _i	T _s	T _m	T _i	
6	1.20	10.3	11.7	79 ^f	275	292		234	279	
8	1.71	12.8	14.0	75 ^f	255	282		217	256	
10	1.21	13.3		78 ^f	270			245		
12	0.73	15.5	18.2	78	236		32	181	215	
14	0.72 ^g	17.6	20.5	91	215	230	62	160	207	
16	0.70 ^g	19.1	21.8	104	190	215	83	162	202	

^a Number of carbon atoms in the side chain

^b In dL/g, measured in CH₂Cl₂/TFA (95/5 (v/v)) at 20 °C

^c Measured at room temperature







^d Measured at 10 °C below the isotropization temperature

^e In °C. Heating and cooling rates: 20 °C/min

^f Transition observed only in the first heating scan

^g In dL/g, measured in CHCl₃/TFA (95/5 (v/v)) at 25 °C

Table 7. Properties of polyesters $\left[\text{O} - \text{C}_6\text{H}_4(\text{R}^1) - \text{O} - \text{C}(=\text{O}) - \text{C}_6\text{H}_4(\text{R}^2) - \text{C}(=\text{O}) \right]_n$

R ¹	R ²	η_{inh} (dl/g)	T _g /°C	T _m /°C	Phase >T _m	Solubility ^{b)}		
						pCP	TCE	CHCl ₃
-CH ₂ - 	-H	1.0	-	380 ^{a)}	-	++	+	-
-(CH ₂) ₂ - 	-H	0.7	-	340	aniso.	++	+	-
-(CH ₂) ₃ - 	-H	4.2	-	325	aniso.	++	+	-
-CH ₂ - 	-Br	2.0	91	(207) ^{c)}	nem.	++	+	-
-(CH ₂) ₂ - 	-Br	2.5	79	(195) ^{c)}	nem.	++	+	-
-(CH ₂) ₃ - 	-Br	1.0	58	(249) ^{c)}	nem.	++	+	++

^a melting in the decomposition range

^b ++: stable solution (>0.5 g/dl) at room temperature

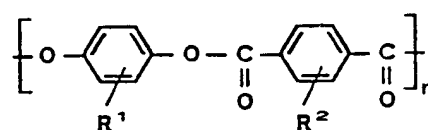
+ : soluble on heating, precipitation on cooling









- : insoluble; pCP: p-chlorophenol,

TCE: 1,1,2,2-tetrachloroethane

^c weak endotherm on annealed samples

Table 8. Properties of polyesters



R ¹	R ²	η_{inh} (dl/g)	T _g ^{a)} °C	T _m ^{a)} °C	Phase >T _m	Solubility ^{b)}		
						pCP	TCE	CHCl ₃
-CH ₂ CH ₂ - 	-CH ₂ CH ₂ - 	0.3-3.6	60	195	nem.	++	++	++
-C(CH ₃) ₃	-CH ₂ CH ₂ - 	0.3-5.0	100	225	nem.	++	++	++
-C(CH ₃) ₃	-Br	0.2-2.6	131	-	-	+	0	-
-C(CH ₃) ₃	-CF ₃	0.3-1.9	141	228	nem.	++	++	++
-O- 	-Cl	1.8	85	241	nem.	++	++	0
-O- 	-Br	0.5-3.0	90	220	nem.	++	++	++
-O- 	-CF ₃	0.35	88	-	iso.	++	++	++
-O- 		0.4-0.7	112	-	iso.	++	++	++

^a products of the highest molecular weights

^b ++: stable solution (>0.5 g/dl) at room temperature


+ : completely soluble on heating

o : partially soluble at elevated temperatures

- : insoluble; pCP: p-chlorophenol,

TCE: 1,1,2,2-tetrachloroethane

Table 9. Polyesters with twisted biphenyl units

$\left[\text{O}-\text{C}_6\text{H}_3(\text{CH}_3)_2-\text{O}-\text{C}(=\text{O})-\text{C}_6\text{H}_3(\text{R})-\text{C}(=\text{O}) \right]_n$		$\left[\text{O}-\text{C}_6\text{H}_3(\text{R})-\text{O}-\text{C}(=\text{O})-\text{C}_6\text{H}_3(\text{CH}_3)_2-\text{C}(=\text{O}) \right]_n$		
1		2		
Polymer	R	$\eta_{\text{inh}}^{\text{a)}$ (dl/g)	T_g T_m Phase (°C)	S o l u b i l i t y ^{b)} pCP TCE CHCl ₃
1	H	1.43	nontractable	+ - -
	Br	1.21	100 230 nem.	+ - -
		1.10	125 - nem.	+ + +
2	CH ₃	0.81	nontractable	+ + -
	tert -Butyl	1.43	150 - nem.	+ + +

^a Measured in p-chlorophenol at 45 °C

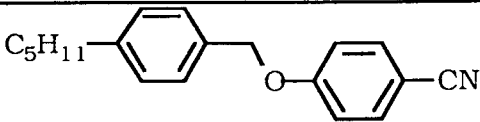
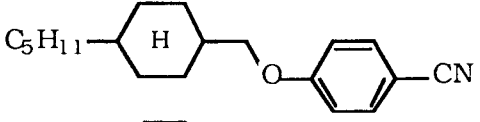
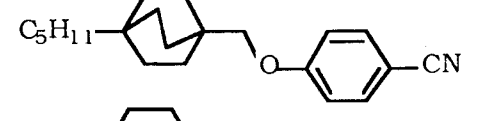
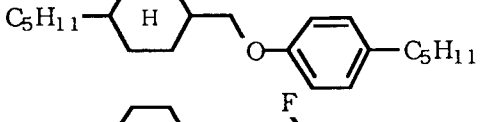
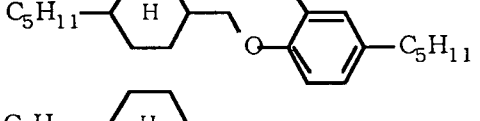
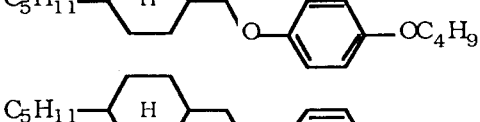
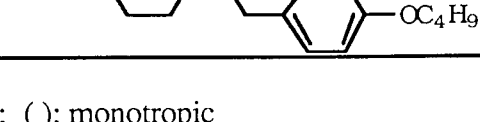
^b ++: stable solution (>0.5 g/dl) at room temperature

+ : soluble on heating, precipitation on cooling

- : insoluble; pCP: p-chlorophenol,

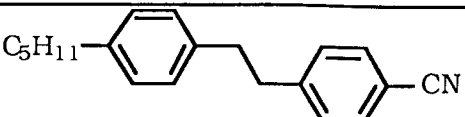
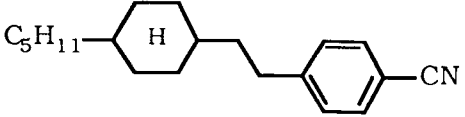
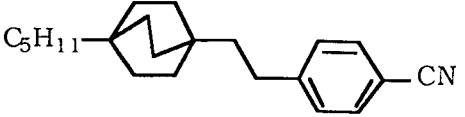
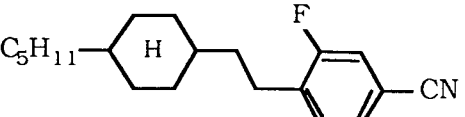
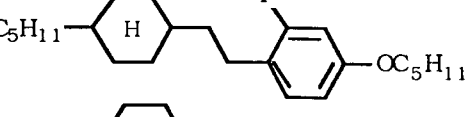
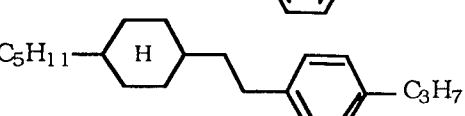
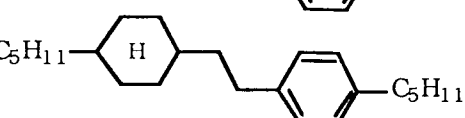
TCE: 1,1,2,2-tetrachloroethane

Table 10. Low molar mass liquid crystals based on benzyl ether and methyleneoxy flexible units (Carr and Gray, 1985; Osman, 1982 A; 1982 B)

No	Structure	Phase transitions (°C)
1		k 49 n [-20] i
2		k 74.3 n (48.6) i
3		k 72 n 73 i
4		k 35 s _B (31) n [21] i
5		k 43 n [-10] i
6		k 55 s _B (47) n (53) i
7		k 22 s _B 44.5 n 45.5 i

[]: virtual; (): monotropic

Table 11. The dependence between structure and phase transitions of some low molar mass liquid crystals based on disubstituted ethane derivatives (Carr et al, 1983; Carr and Gray, 1985; Kelly and Schadt, 1984; Osman and Ba, 1983; Praefke et al, 1980; Schadt et al, 1983)

No	Structure	Phase transitions (°C)
8		k 62 n [-24] i
9		k 30 n 51 i
10		k 76 n 113 i
11		k 45 n 54 i
12		k 26 n (12) i
13		k 4 s _B 18 i
14		k 46 s _B 109 i

[]: virtual; (): monotropic

Table 12. Thermodynamic Parameters Corresponding to the Orientational and Conformational Order Contributions of HMS-X (Percec et al, 1991 M), MBPE-X (Percec and Tsuda, 1990 D), CIBPE-X (Zuber, 1991), and of Polyesters Based on 4,4'-Dihydroxy-2,2'-Dimethylazoxybenzene and α,ω -Alkanedioic Acids (DMAB-X) (Blumstein and Blumstein, 1988).

Nature of Order	<u>(ΔH_{in})even (kcal/mru)</u>				<u>(ΔH_{in})odd (kcal/mru)</u>			
	HMS-X	MBPE-X	CIBPE-X	DMAB-X	HMS-X	MBPE-X	CIBPE-X	DMAB-X
Orientational/ mole of mesogen	1.45	2.00	1.63	1.12	0.34	0.30	0.20	0.22
Conformational/ mole of -CH ₂ -	0.03	0.01	0.03	0.38	0.04	0.03	0.04	0.045
Nature of Order	<u>(ΔS_{in})even (cal/mol^oK)</u>				<u>(ΔS_{in})odd (cal/mol^oK)</u>			
	HMS-X	MBPE-X	CIBPE-X	DMAB-X	HMS-X	MBPE-X	CIBPE-X	DMAB-X
Orientational/ mole of mesogen	2.15	4.02	3.60	1.80	0.45	0.85	0.62	0.34
Conformational/ mole of -CH ₂ -	0.15	0.17	0.12	0.21	0.13	0.11	0.07	0.14

Table 13. Thermal Transitions (°C) and Corresponding Thermodynamic Parameters, ΔH_{in} (kcal/mru) and ΔS_{in} (cal/mru °K)^a of 1-(4-Methoxyphenyl)-2-(2-R-4-methoxyphenyl) (RBMPE) and 1-(4-Hydroxyphenyl)-2-(2-R-hydroxyphenyl)ethane (RBPE) and of the corresponding RBPE-8 and RBPE-5 polymers. Van der Waal's Radius of R (Å) and Electronegativity of R, Ar-R bond length (Å), and breadth of molecule (Å)

R	RMBPE	RBPE	Radius of R	Electronegativity of R	Breadth of RBPE	Ar-R Bond Length	T _{ni}	T _{in}	ΔH_{in}	ΔS_{in}	T _{in}	ΔH_{in}	ΔS_{in}
H	125-127	200 ^b	1.2	2.19	6.69	1.4	155	146	--	--	--	--	--
F	73-74	172-173	1.35	4.0	7.03	1.30	165	152	2.82	6.8	92	0.92	2.5
Cl	62-64	126	1.8	3.0	7.82	1.70	130	118	2.27	5.83	52	0.65	2.0
Br	81-82	114-115	1.95	2.8	8.10	1.85	111	102	2.12	5.3	47	0.59	1.86
CH ₃	52-54	148	2.0	2.3	7.76	1.33	132	119	2.33	5.9	38	0.49	1.57
CF ₃	69-70	64-65	2.3	3.29	8.15	1.33	76	43	0.93	2.94	--	--	--

^a Data from Percec and Zuber, 1992 H

Table 14. Characterization of Hyperbranched Polyethers Based on TPD-b with Different Tail Lengths R. Data Collected from Second Heating and First Cooling DSC Scans (Percec and Kawasumi, 1992 L).

Tail	Yield (%)	(Mn)GPC	(Mw/Mn)GPC	thermal transitions (°C) and corresponding enthalpy changes (Kcal/mru) in parentheses	
R				Heating	Cooling
Octyl	80.0	7900	2.6	g 20 n 40 (0.75) i	i 30 (70.0) n 15 g
Hexyl	82.2	4700	3.9	g 24 n 39 (0.15) i	i 30 (0.18) n 18 g
Butyl	70.3	4400	3.5	g 40 i	i 34 g
Benzyl	79.2	4700	3.8	g 48 n 60 (0.10) i	i 53 (0.15) n 43 g

Table 15. Synthesis and Characterization of Hyperbranched Polymers and Comparison of Their Phase Behavior with That of the Linear Model Polyether (TPD-8).^a

Polymer	Yield (%)	Mn (GPC)	Mw/Mn (GPC)	thermal transitions (°C) and corresponding enthalpy changes (KJ/mru), in parentheses	
				Heating	Cooling
TPD-b-8 ^b	80.0	7900	2.60	g 19 n 37 (2.41) i	i 25 (-2.17) n 10 g
TPH-b-Bz ^c	94.1	2520	1.69	g 47 i	i 39 g
TPH-b-4	71.9	3140	1.51	g 42 n 48 (0.12) i	i 33 g
TPH-b-6	65.1	3170	1.57	g 29 n 40 (0.20) i	i 33 (-0.08) n 22 g
TPH-b-8	75.7	3220	1.58	g 24 n 41 (1.85) i	i 30 (-1.82) n 15 g
BPNT-b-8 ^d	71.5	8640	2.49	g 27 n 59 (1.89) i	i 49 (-2.51) n 18 g
TPT-b-8 ^e	79.9	11800	2.42	g 50 n 132 (2.96) i	i 125 (-2.88) n 38 g
TPT-b-All	81.4	8333	1.90	k 126 (7.59) n 155 (3.46)	i 149 (-2.90) n 166 (-6.98) k
TPD-8 ^f	92.2	27500	2.00	g 19 n 60 (6.61) i	i 47 (-6.61) n 13 g

^a Yields are after precipitation in methanol. Molecular weights and thermal transitions are after precipitation in acetone.

All thermal data are collected from second heating and first cooling DSC scans.

^b TPD-b-X = short name for the polymer derived from 10-bromo-1-(4-hydroxy-4'-biphenyl)-2-(4-hydroxyphenyl)decane (See Percec et al, 1994 G).

^c TPH-b-X = polymer derived from 8.

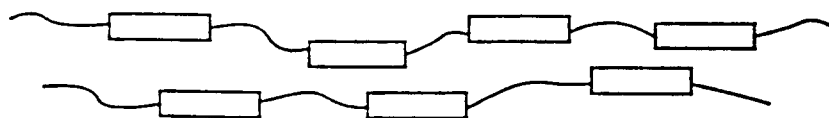
^d BPNT-b-X = polymer derived from 22.

^e TPT-b-X = polymer derived from 30.

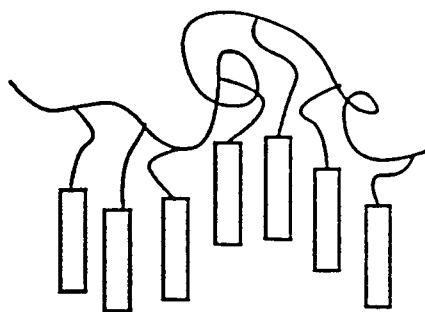
^f TPD-8 = linear polymer from 1-(4-hydroxy-4'-biphenyl)-2-(4-hydroxyphenyl)decane and 1,8-dibromooctane (See Percec et al, 1994 G).

Table 16. Phase Transitions of $G_1(X)$ to $G_4(X)$ from Schemes 34 to 36
(k=crystalline, i=isotropic, n=nematic, g=glassy, X=unknown).

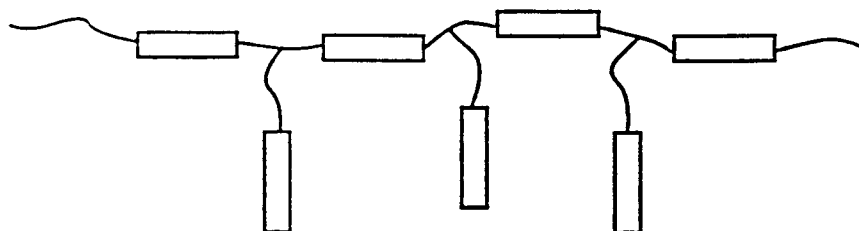
$G_1(\text{Br})$		k 64 i	i 51 n 40 k
$G_2(\text{OH})$		X 62 n 92 i	i 85 n 47 X
$G_3(\text{OH})$		X 69 n 105 i	i 98 n 57 X
$G_3(\text{Br})$	g 52	X 72 n 104 i	i 97 n 64 X
$G_4(\text{OH})$	g 62	X 74 n 110 i	i 103 n 59 X



MAIN CHAIN LIQUID CRYSTAL
POLYMERS



SIDE CHAIN LIQUID CRYSTAL
POLYMERS



COMBINED LIQUID CRYSTAL
POLYMERS

Figure 1

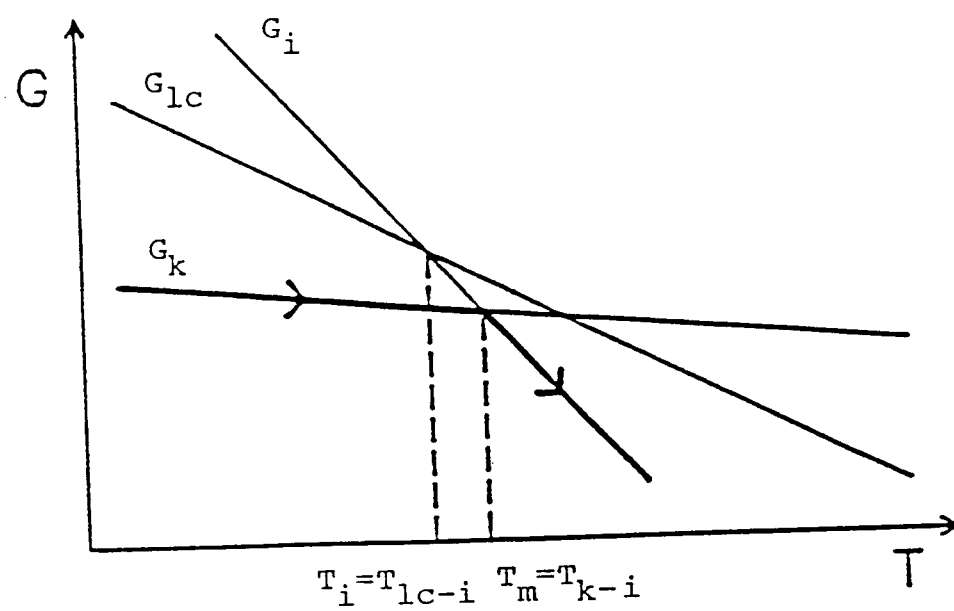


Figure 2

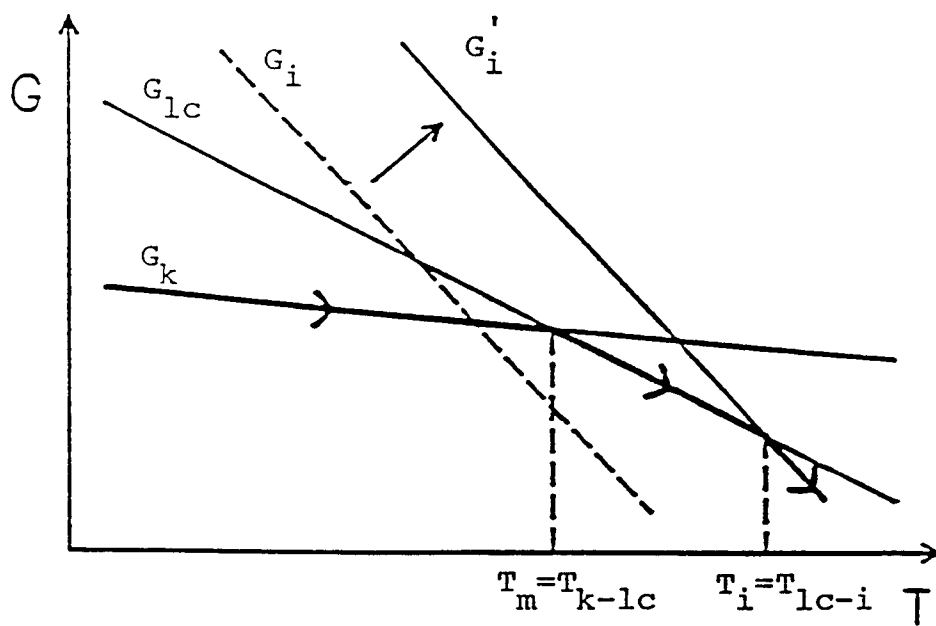


Figure 3

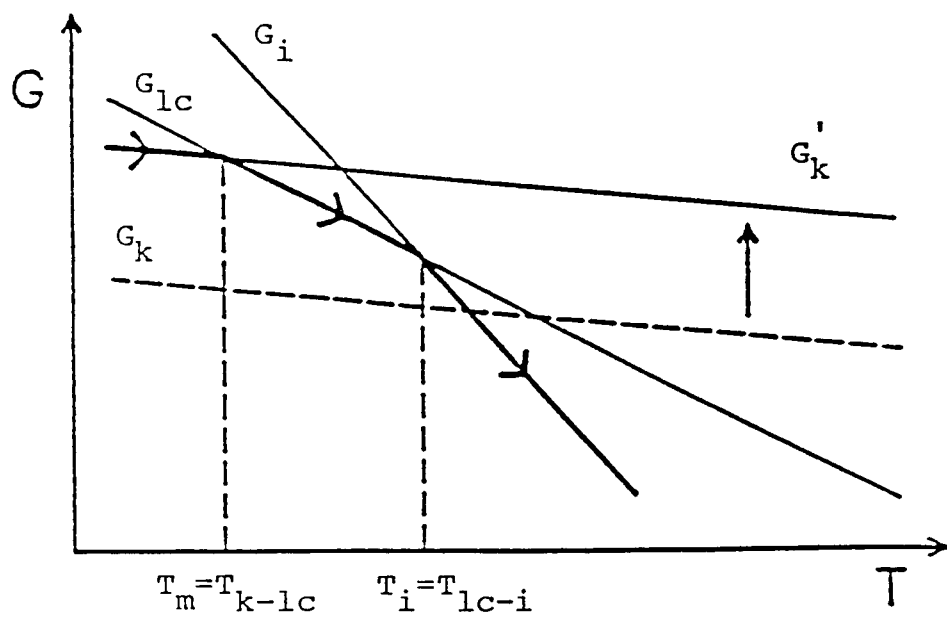


Figure 4

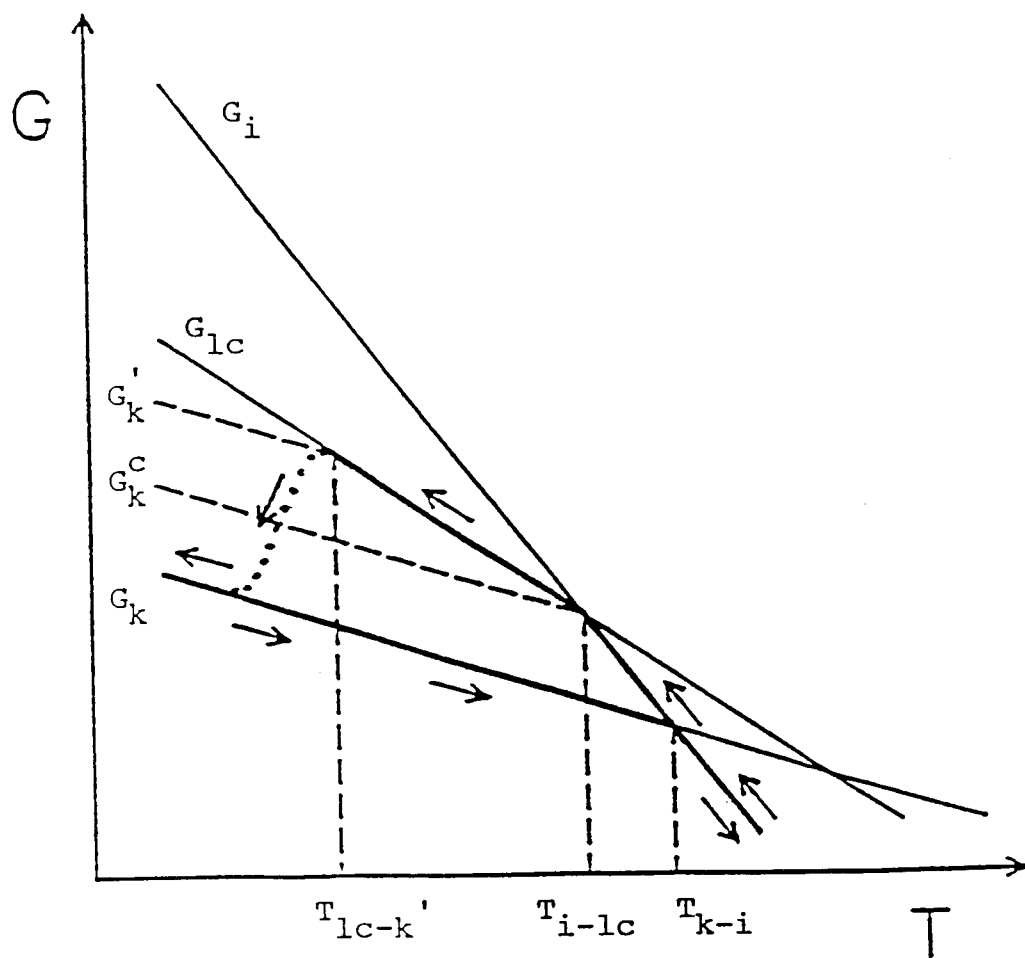


Figure 5

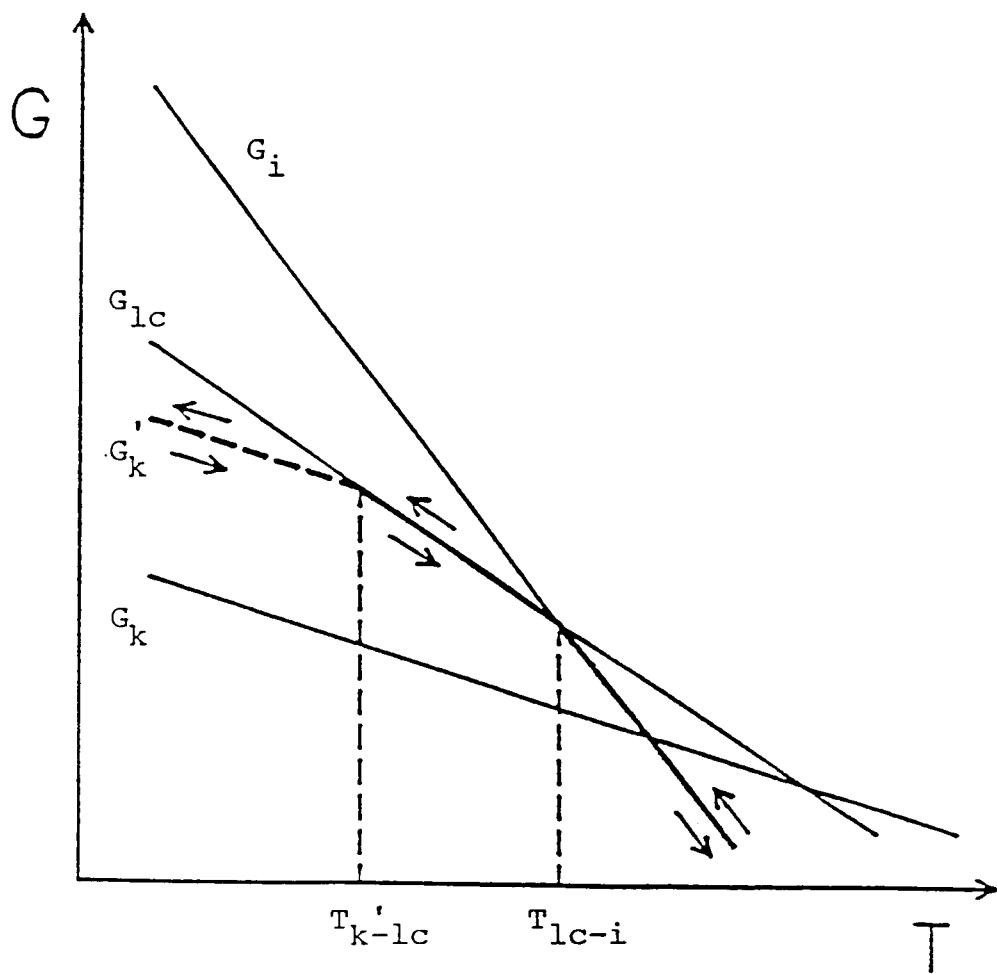


Figure 6

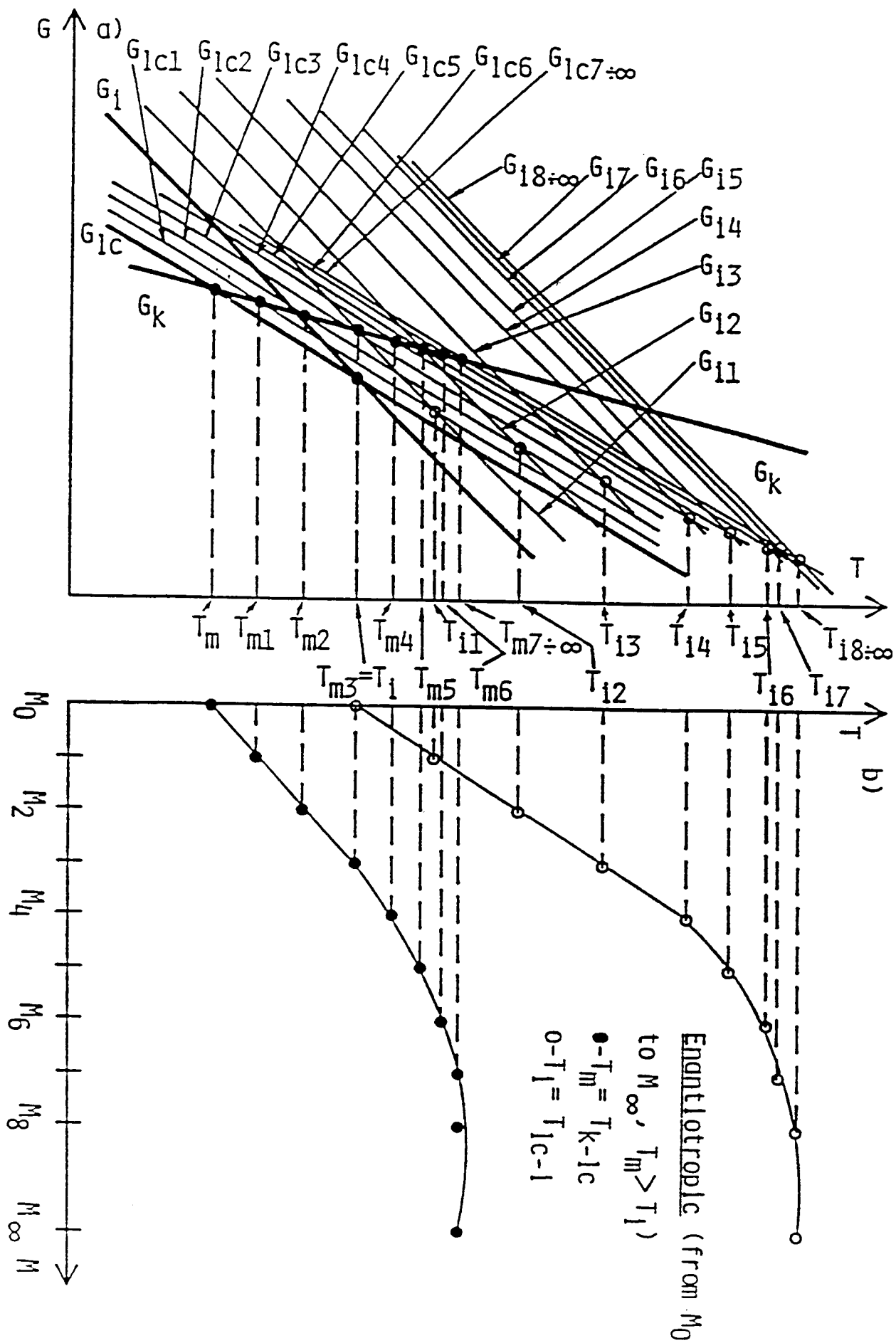


Figure 7

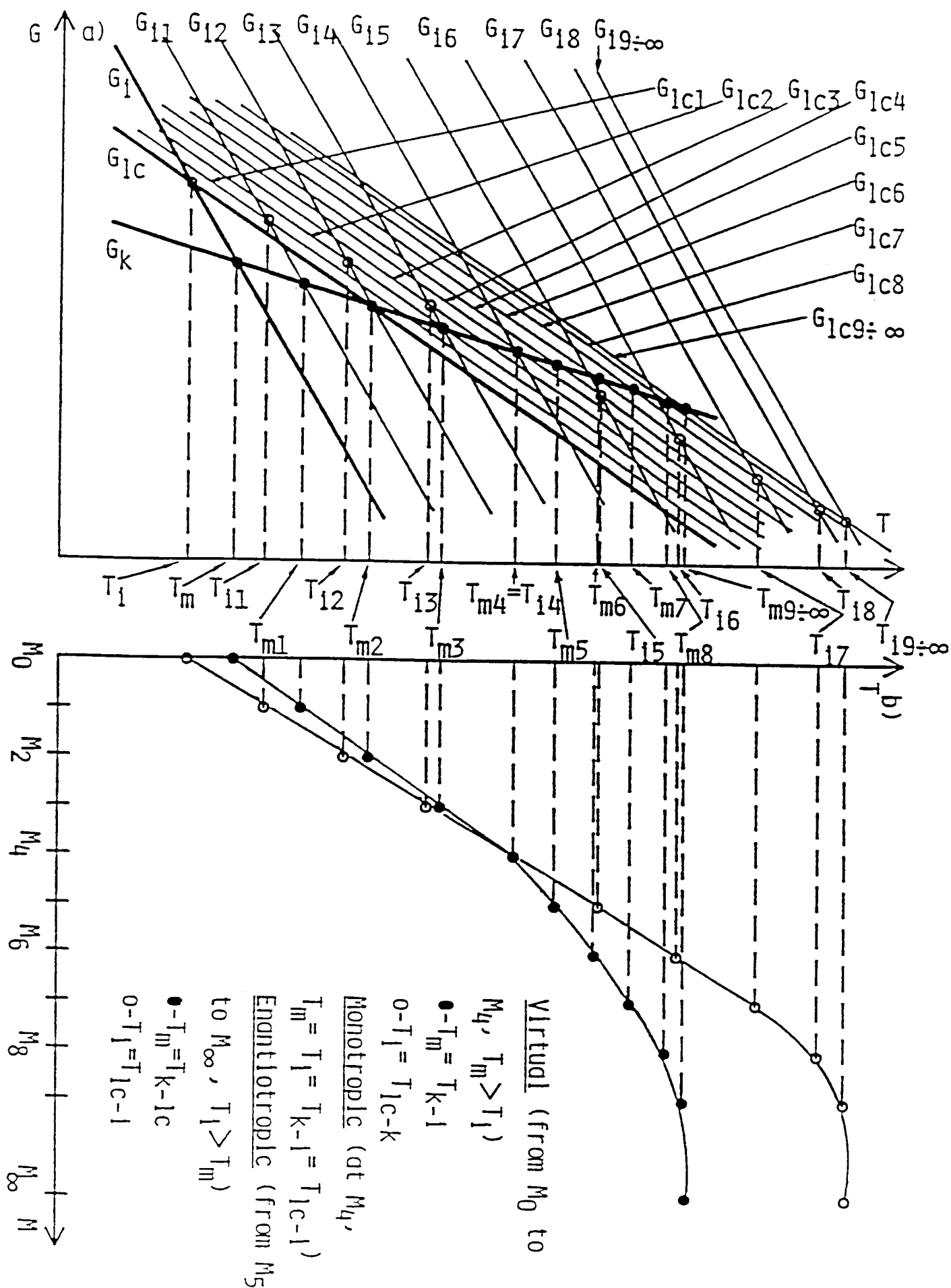


Figure 8

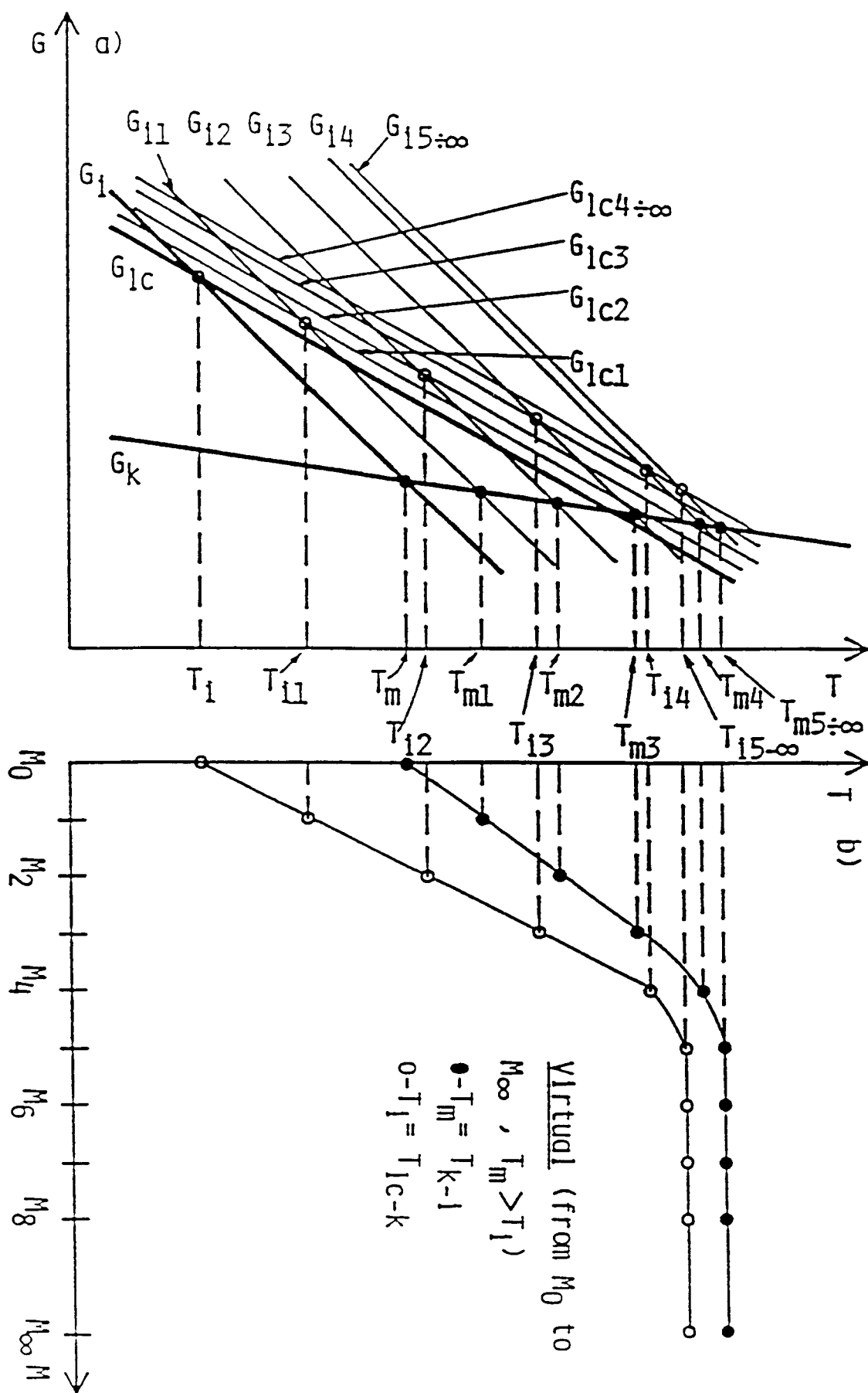


Figure 9

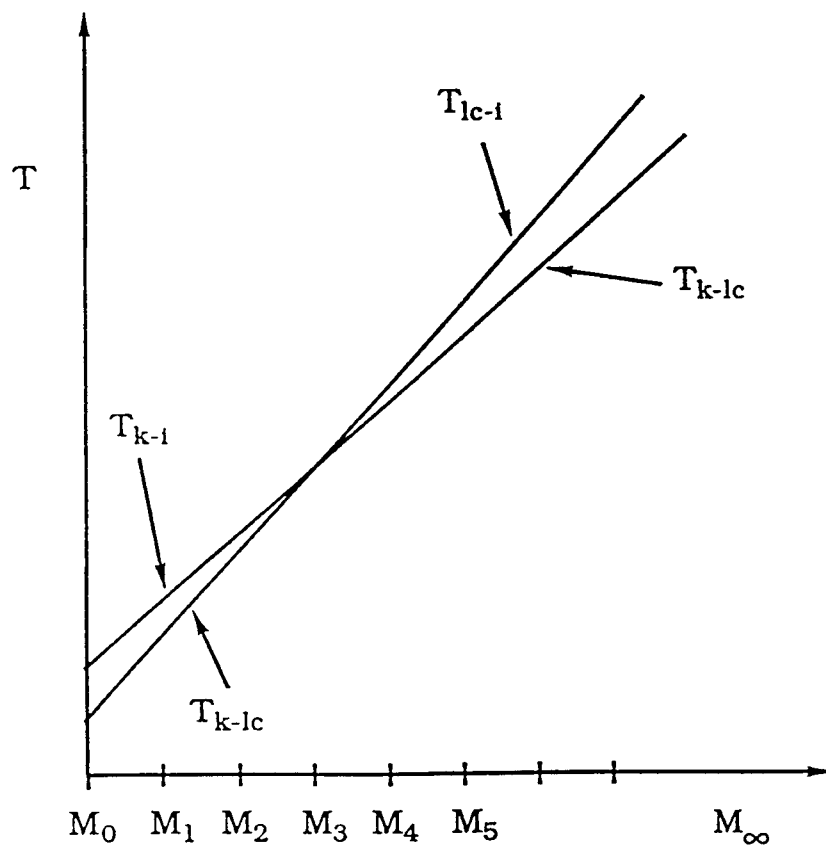
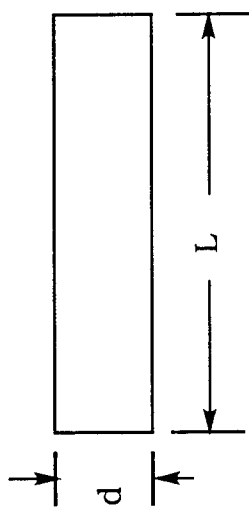
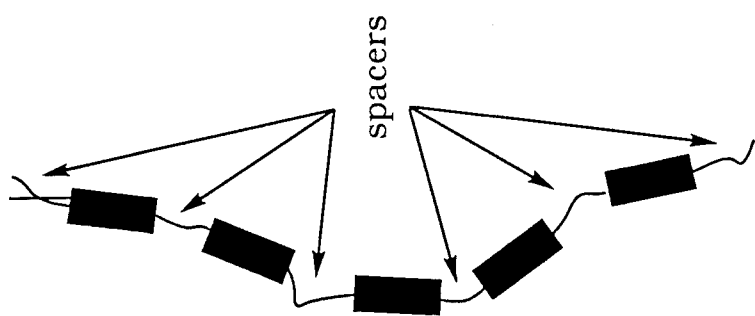
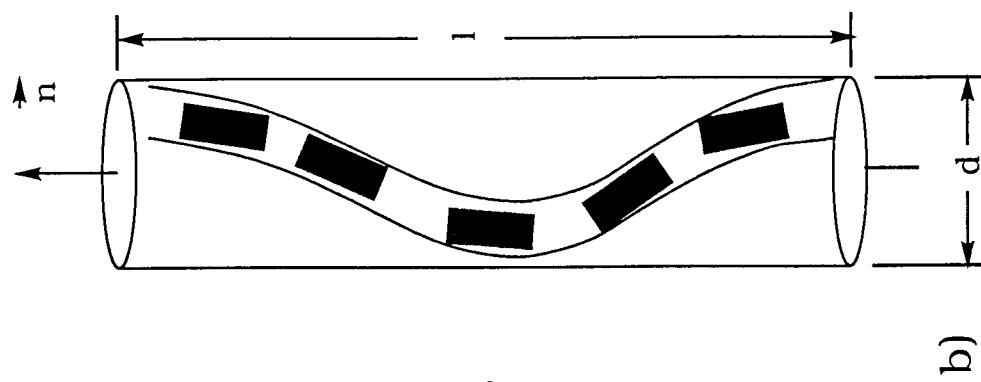


Figure 10



axial ratio $x = L/d$

a)

Figure 11

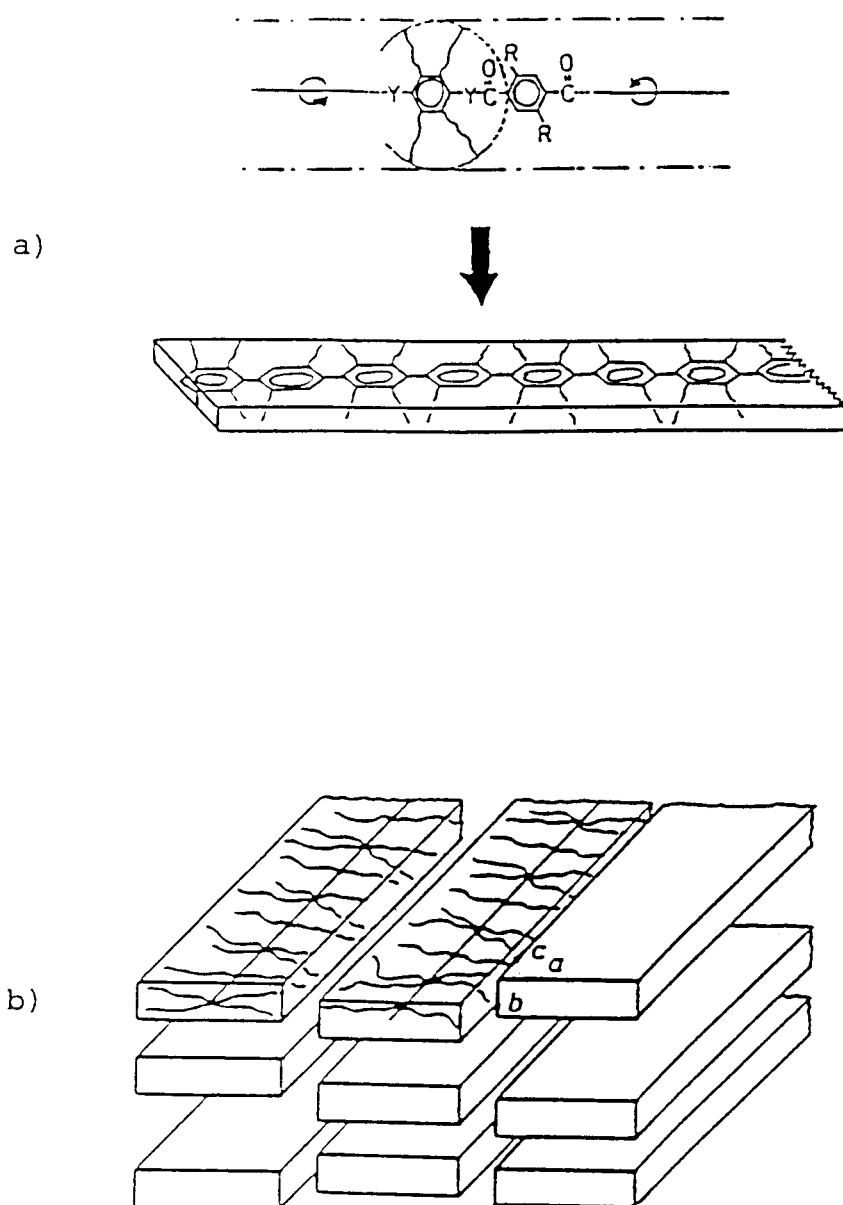
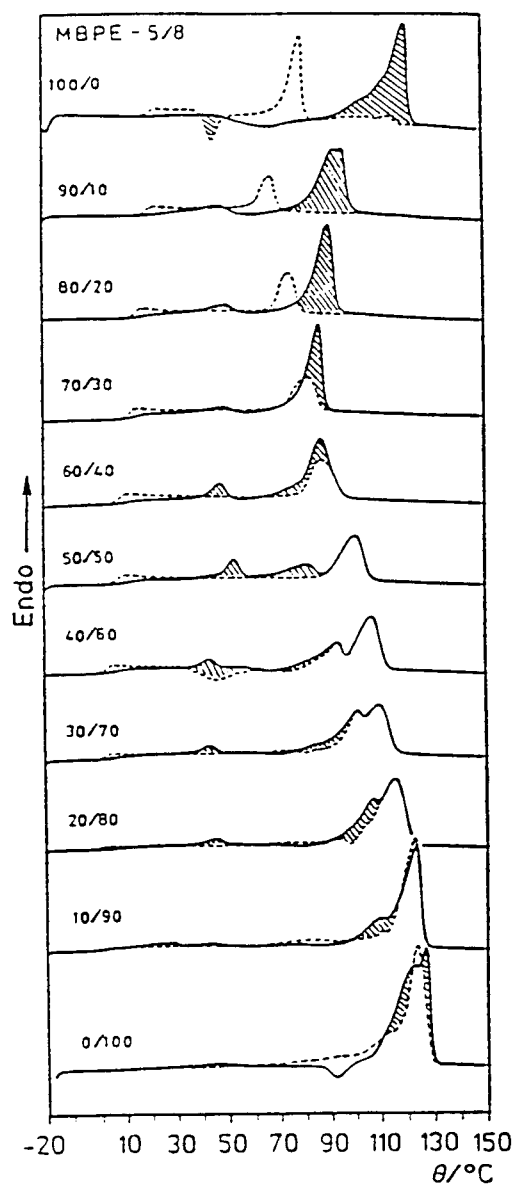
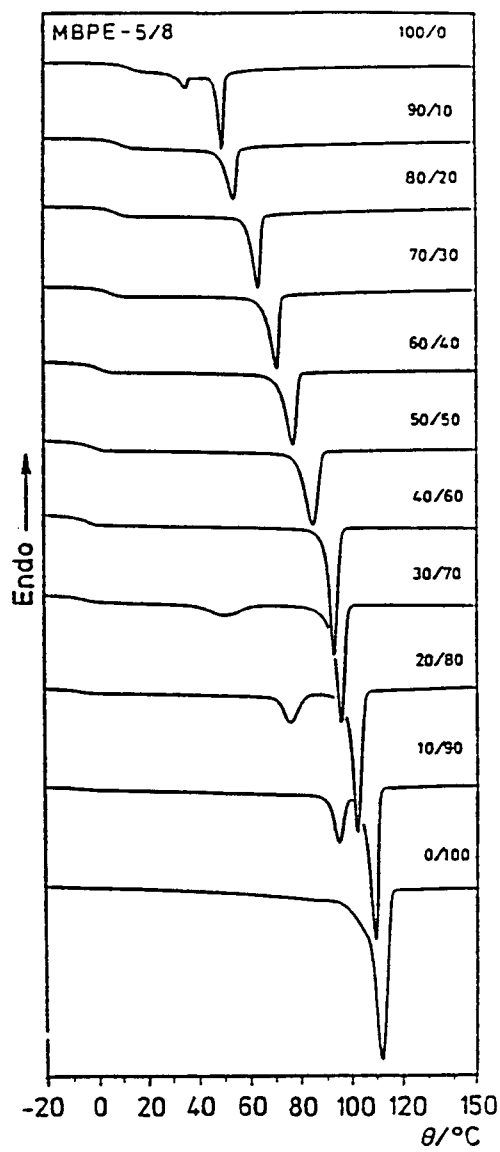


Figure 12

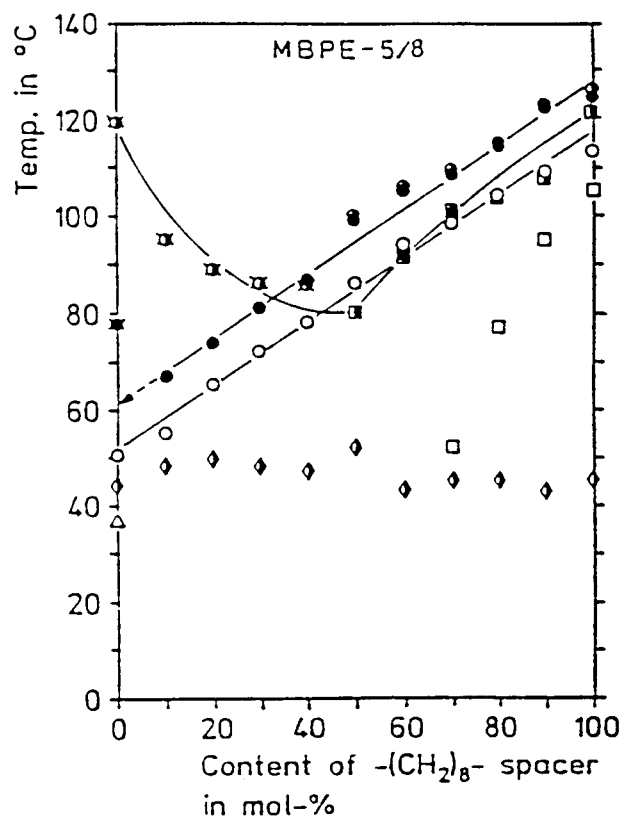


a)

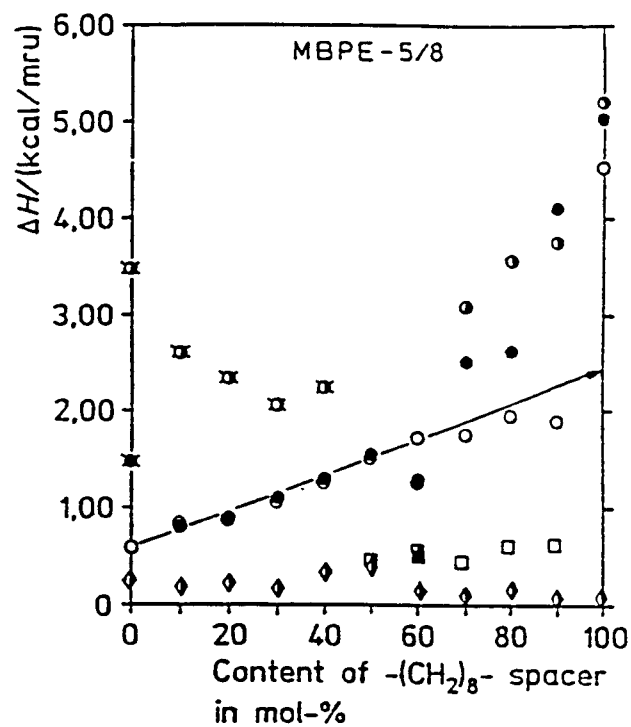


b)

Figure 13



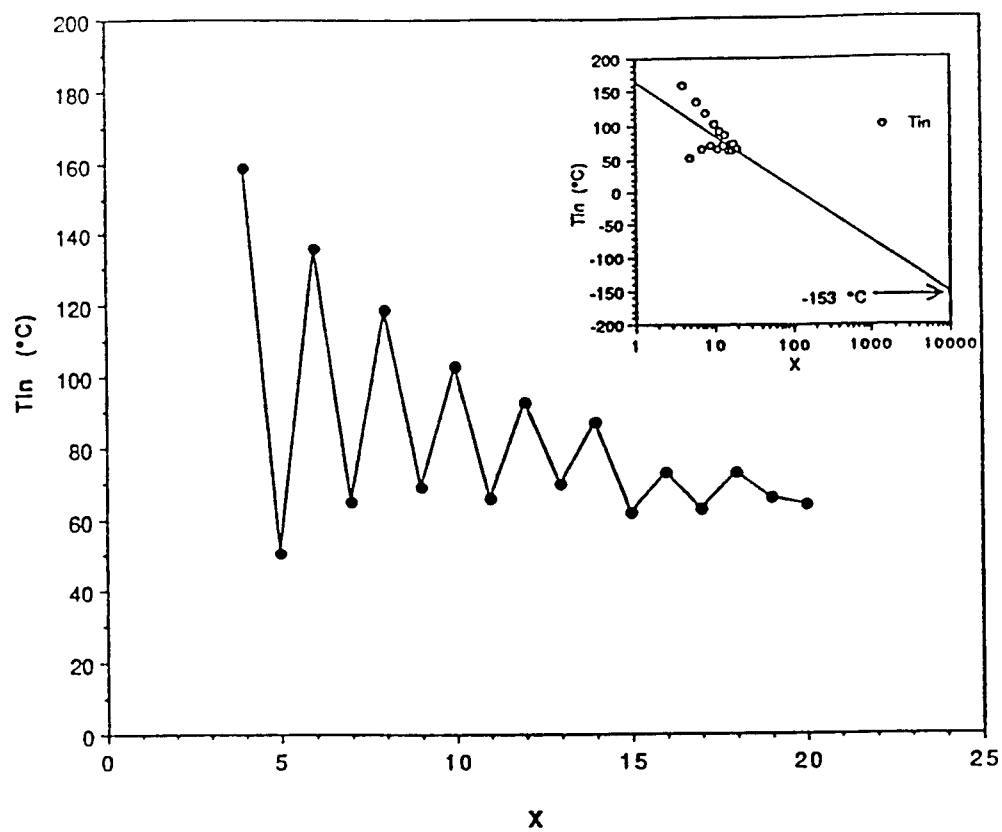
a)



b)

Figure 14

a)



b)

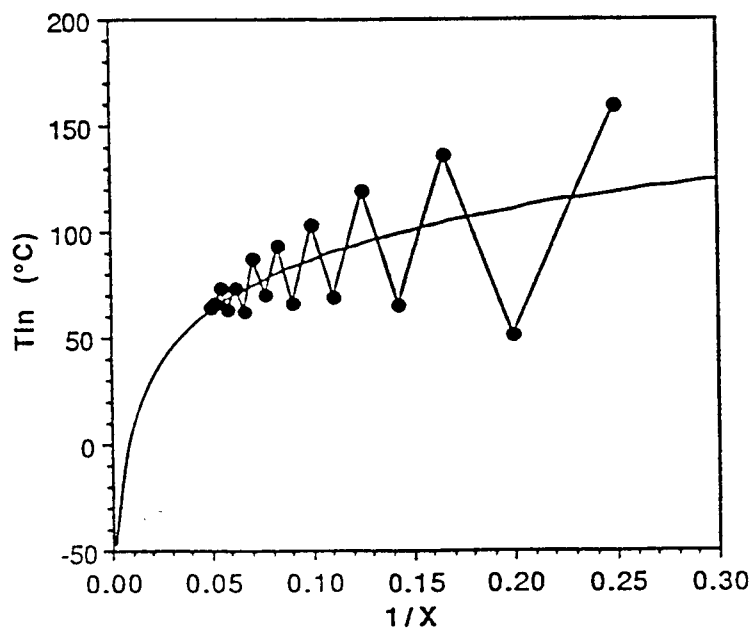
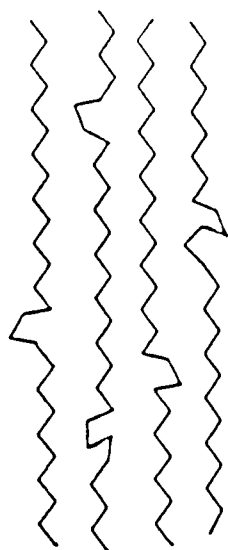
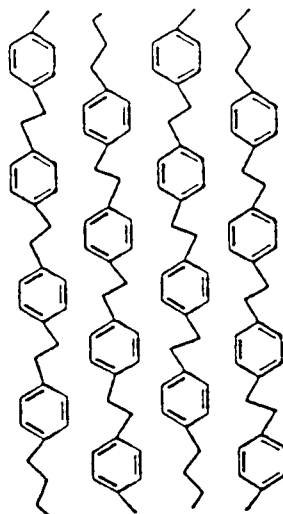


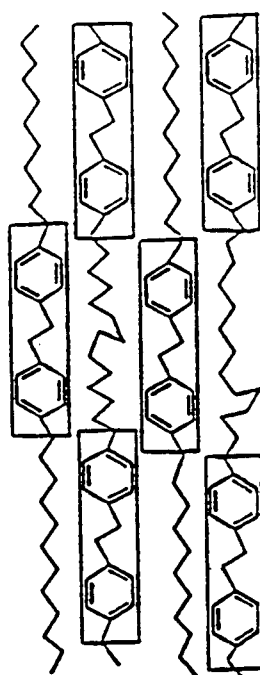
Figure 15



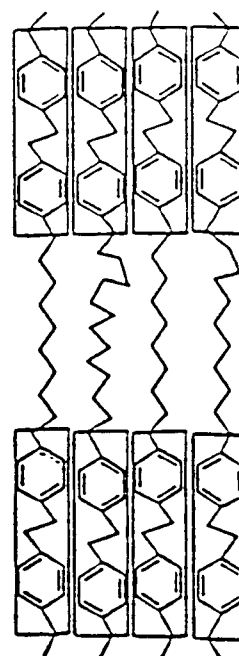
PE
columnar



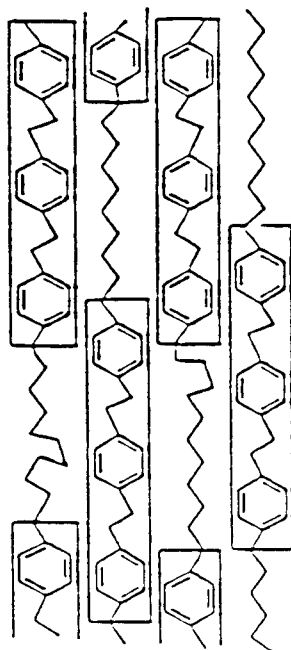
PX
columnar



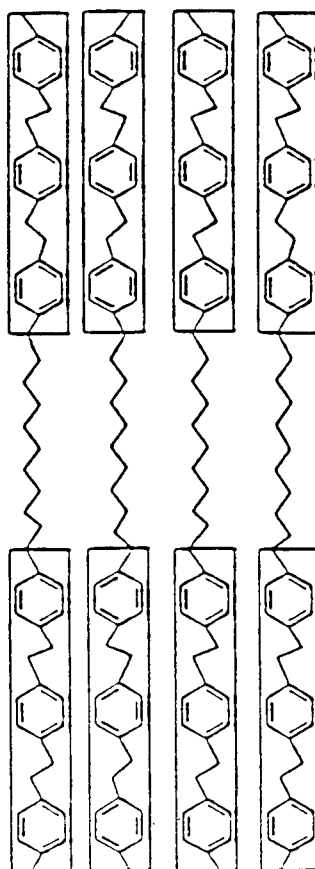
BPE-8/12
columnar



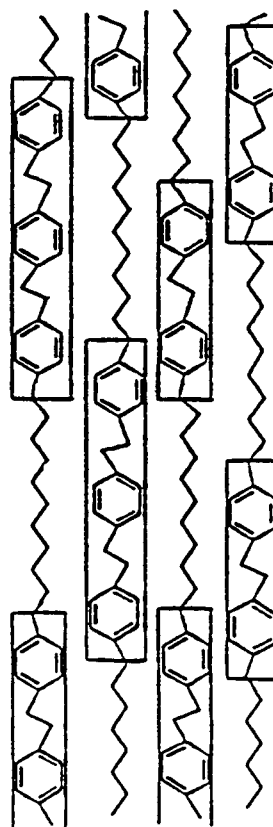
BPE-8/12
Sb



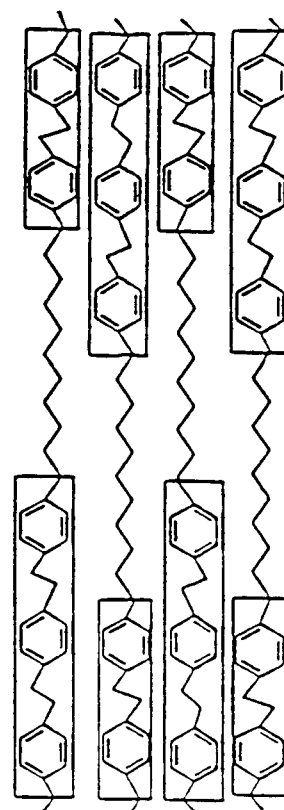
PEB-9
columnar



PEB-9
Sb

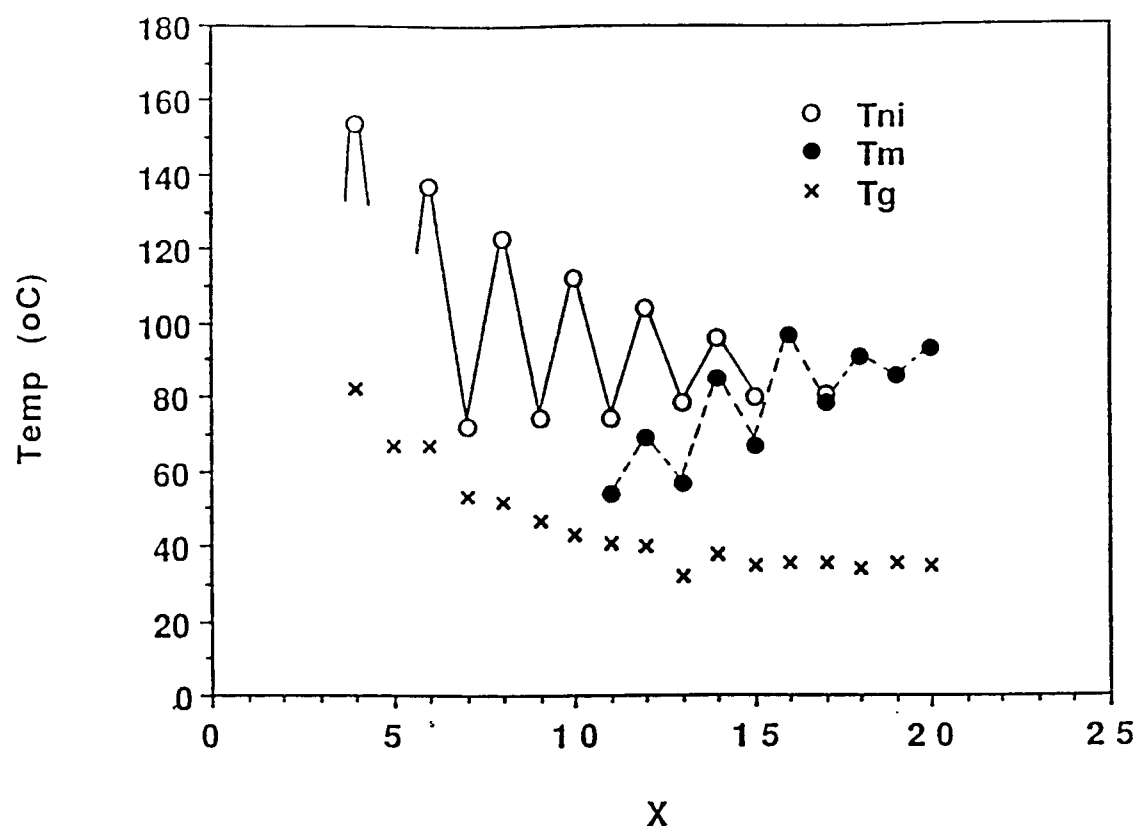


BPE/PEB(A/B)-9
columnar



BPE/PEB(A/B)-9
smectic

a)



b)

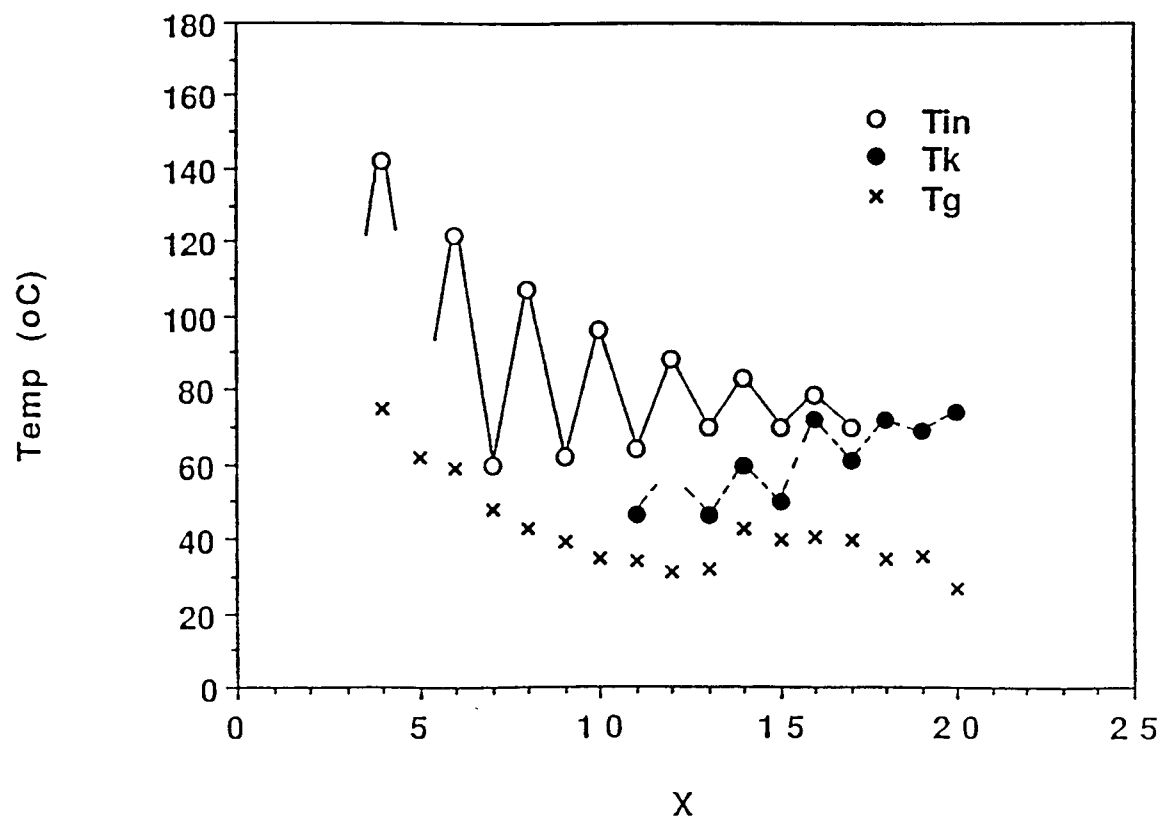


Figure 17

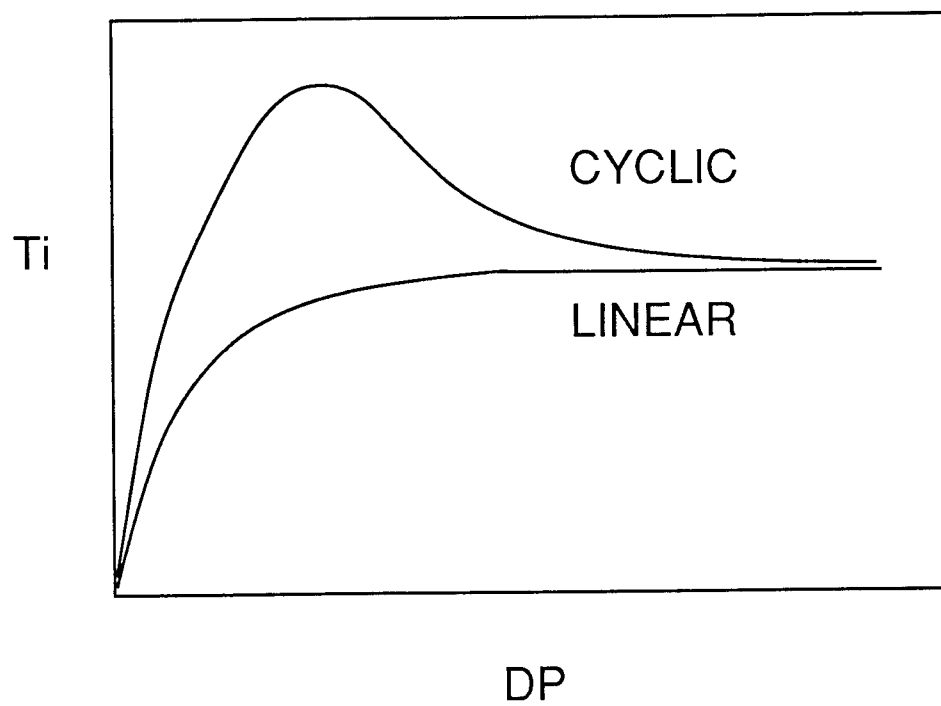


Figure 18

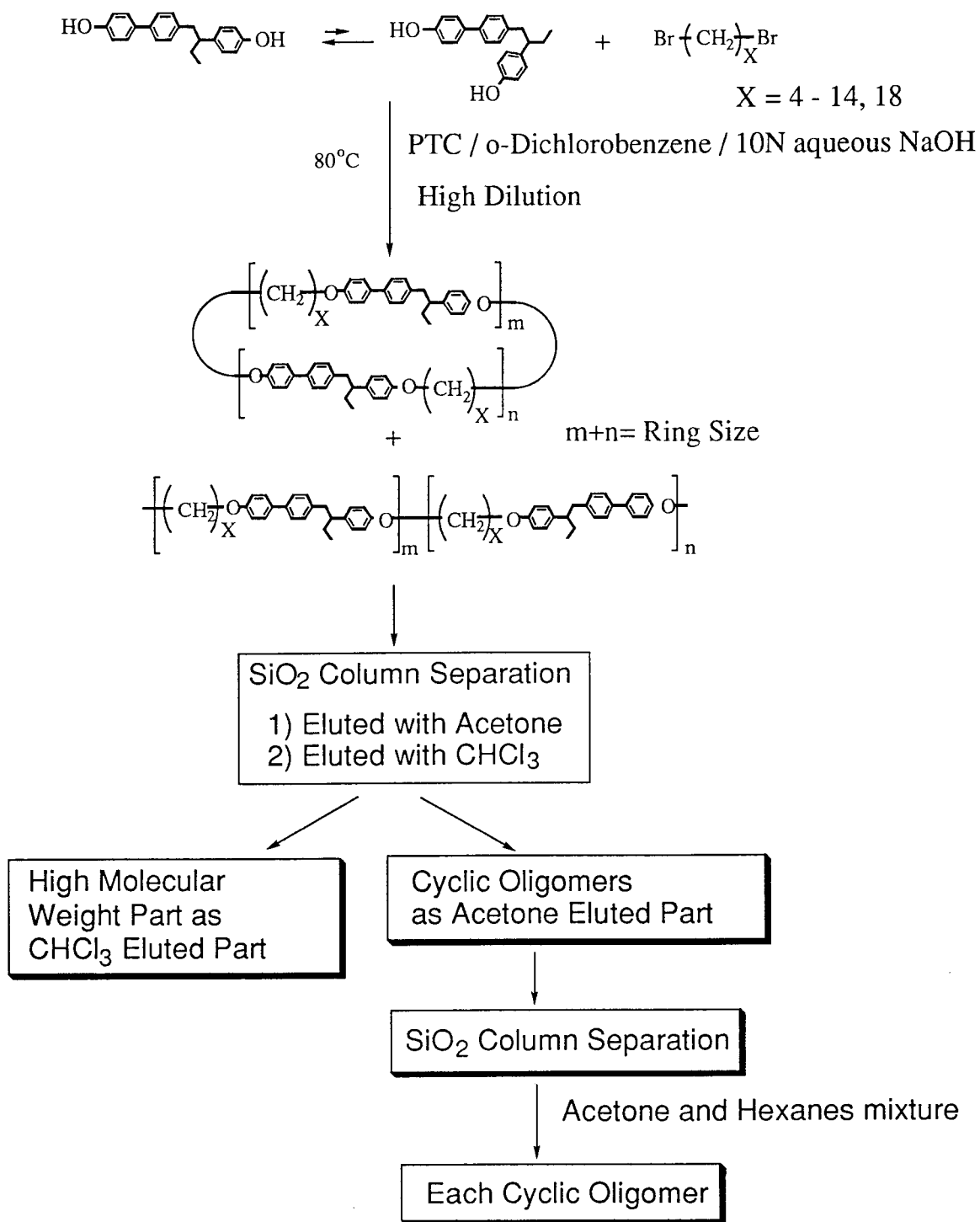


Figure 19

$$\text{CH}_3(\text{CH}_2)_9\text{O}-\text{C}_6\text{H}_4-\text{C}_6\text{H}_4-\text{CH}_2\text{CH}_2-\text{C}_6\text{H}_4-\text{O}(\text{CH}_2)_9\text{CH}_3$$
$$\begin{array}{c} \text{CH}_3(\text{CH}_2)_9\text{O}-\text{C}_6\text{H}_4-\text{CH}_2\text{CH}_2-\text{C}_6\text{H}_4-\text{O}(\text{CH}_2)_{10}\text{O}-\text{C}_6\text{H}_4-\text{CH}_2\text{CH}_2-\text{C}_6\text{H}_4-\text{O}(\text{CH}_2)_9\text{CH}_3 \\ \text{CH}_3(\text{CH}_2)_9\text{O}-\text{C}_6\text{H}_4-\text{C}_6\text{H}_4-\text{CH}_2\text{CH}_2-\text{C}_6\text{H}_4\text{O}(\text{CH}_2)_{10}\text{O}-\text{C}_6\text{H}_4-\text{C}_6\text{H}_4-\text{CH}_2\text{CH}_2-\text{C}_6\text{H}_4\text{O}(\text{CH}_2)_9\text{CH}_3 \\ \text{CH}_3(\text{CH}_2)_9\text{O}-\text{C}_6\text{H}_4-\text{C}_6\text{H}_4-\text{CH}_2\text{CH}_2-\text{C}_6\text{H}_4\text{O}(\text{CH}_2)_{10}\text{O}-\text{C}_6\text{H}_4-\text{CH}_2\text{CH}_2-\text{C}_6\text{H}_4-\text{C}_6\text{H}_4\text{O}(\text{CH}_2)_9\text{CH}_3 \end{array}$$

$\text{CH}_3(\text{CH}_2)_9\text{O}-\text{C}_6\text{H}_4-\text{C}_6\text{H}_4-\text{CH}(\text{C}_2\text{H}_5)-\text{C}_6\text{H}_4-\text{O}$ Trimers
 $(\text{CH}_2)_{10}\text{O}-\text{C}_6\text{H}_4-\text{C}_6\text{H}_4-\text{CH}(\text{C}_2\text{H}_5)-\text{C}_6\text{H}_4-\text{O}-(\text{CH}_2)_{10}$
 + Constitutional Isomers
 $\text{O}-\text{C}_6\text{H}_4-\text{C}_6\text{H}_4-\text{CH}(\text{C}_2\text{H}_5)-\text{C}_6\text{H}_4-\text{O}-(\text{CH}_2)_9\text{CH}_3$

Chemical structures of the monomers used in the synthesis of the poly(ether)s. The structures include:

- Tetramers:** A central structure consisting of a 4,4'-biphenyl core linked by a 1,3-phenylene group, with two 4-ethoxyphenyl groups attached at the 2 and 2' positions.
- + Constitutional Isomers:** A structure showing a 4,4'-biphenyl core linked by a 1,3-phenylene group, with two 4-ethoxyphenyl groups attached at the 2 and 2' positions, and a 4-ethoxyphenyl group attached at the 4' position.

Figure 20

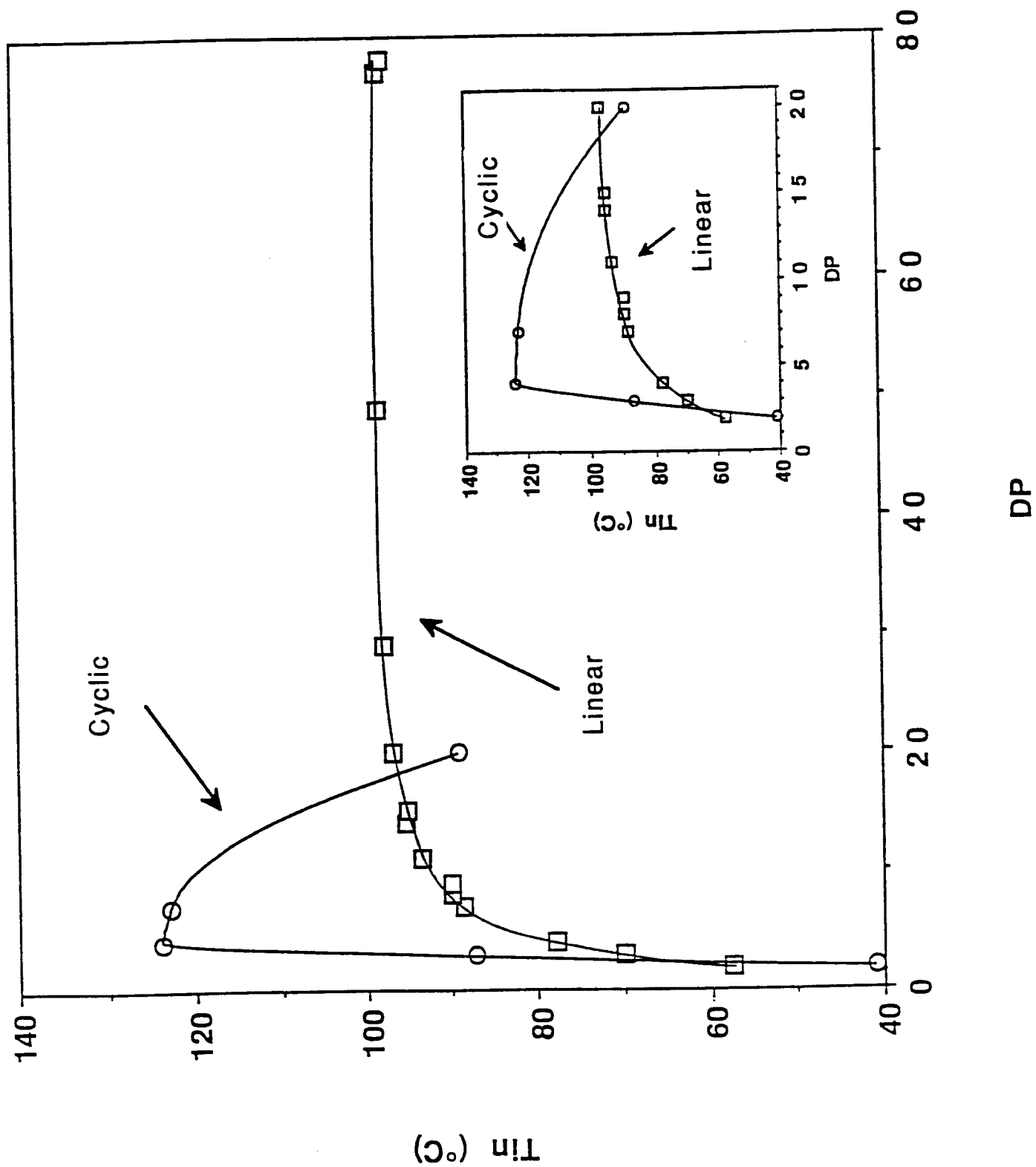


Figure 21

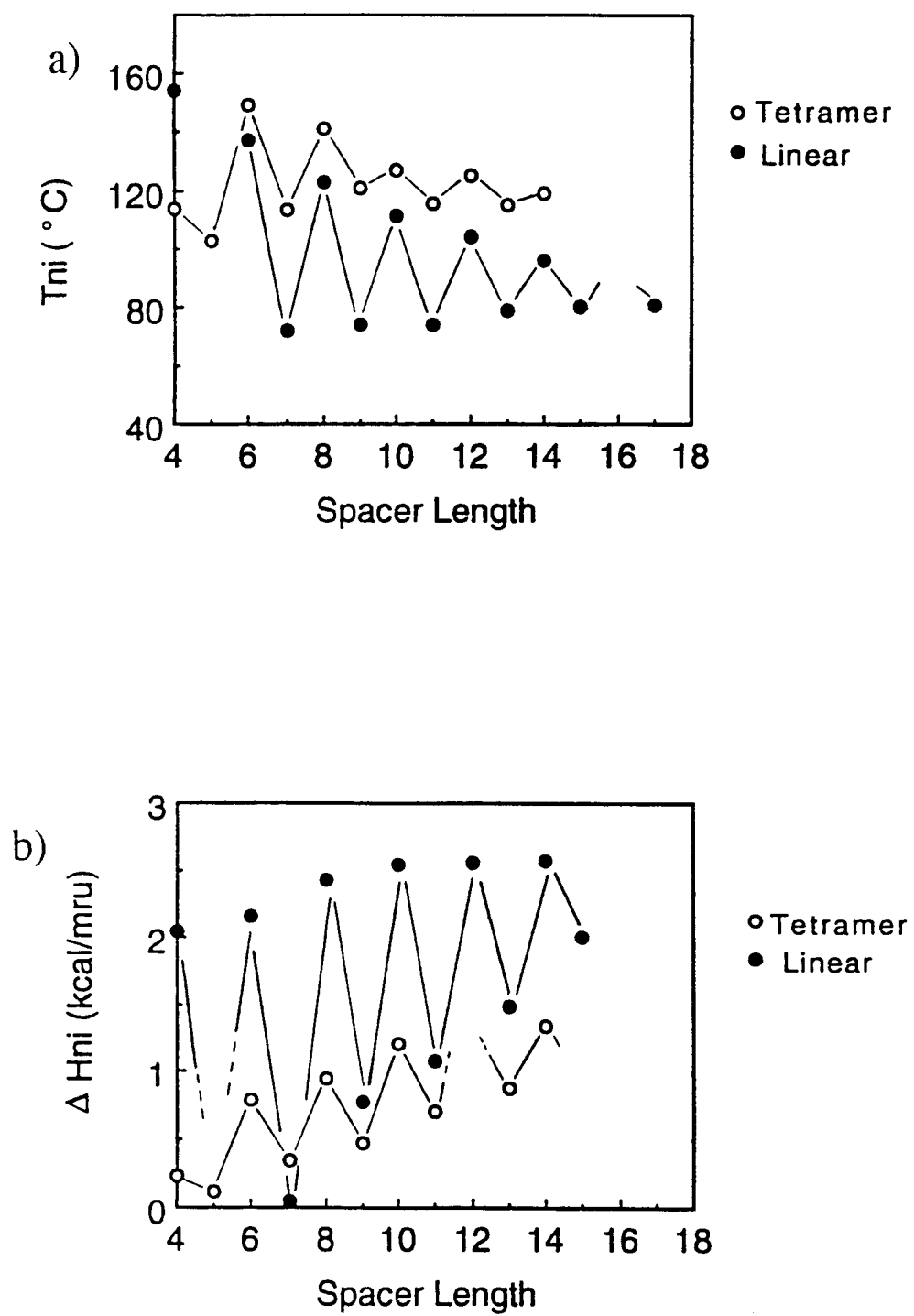


Figure 22

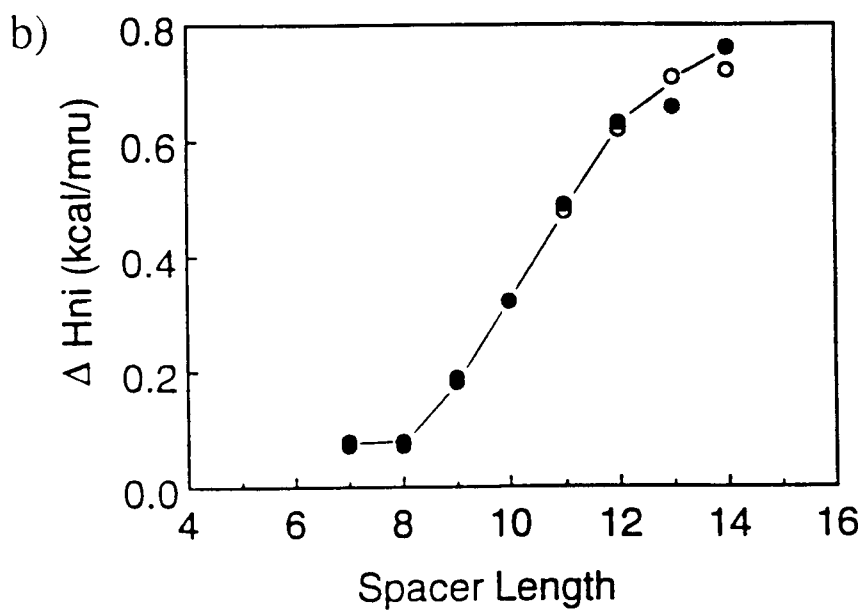
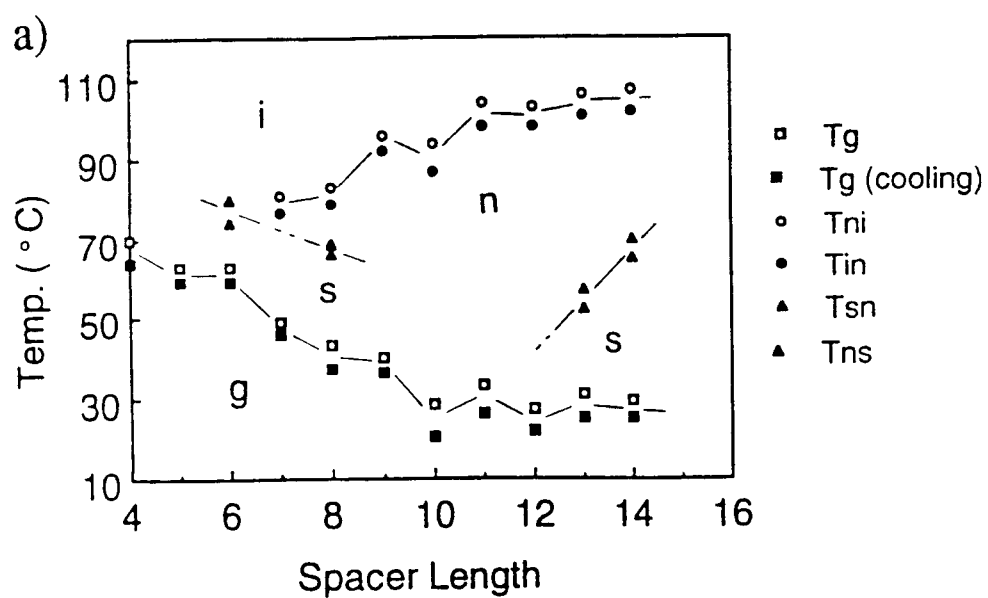


Figure 23

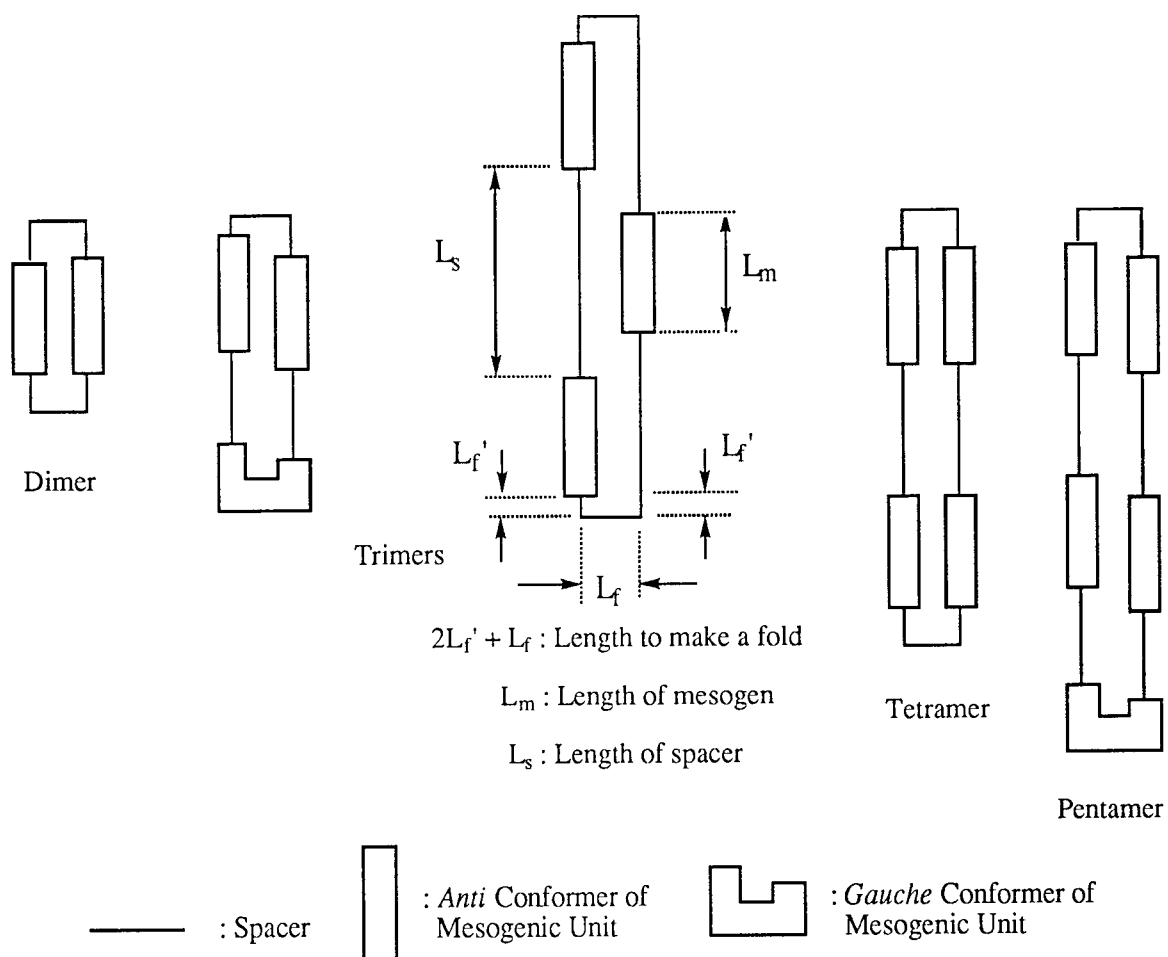


Figure 24

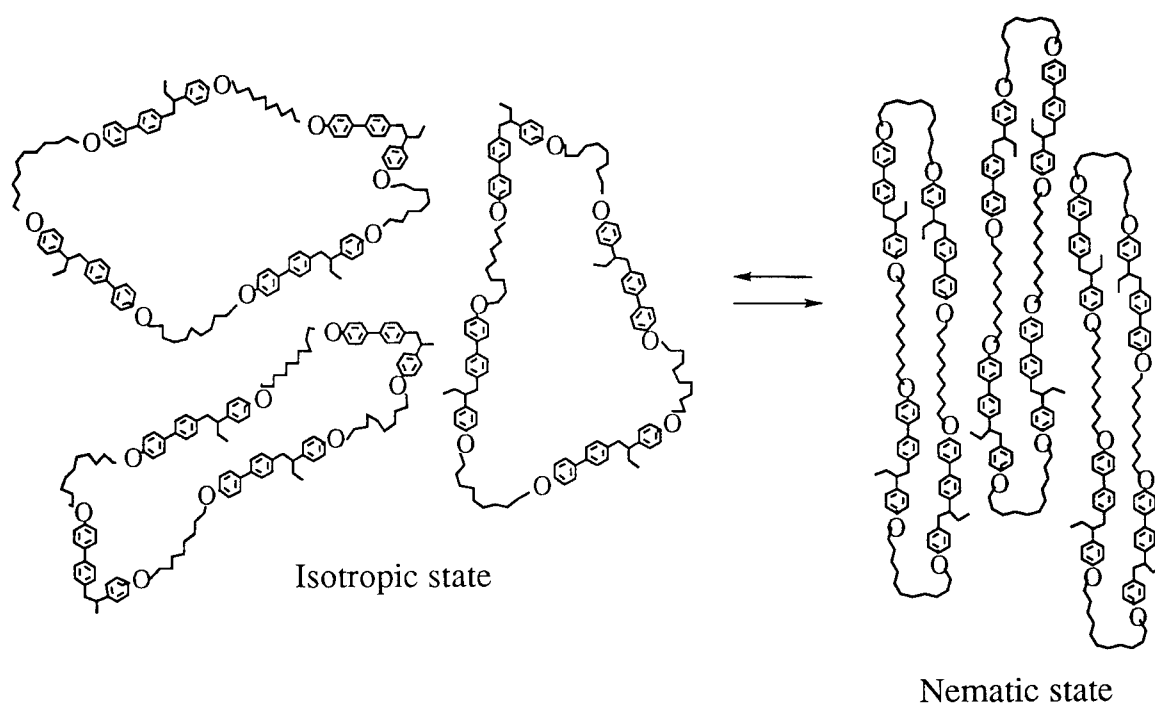


Figure 25

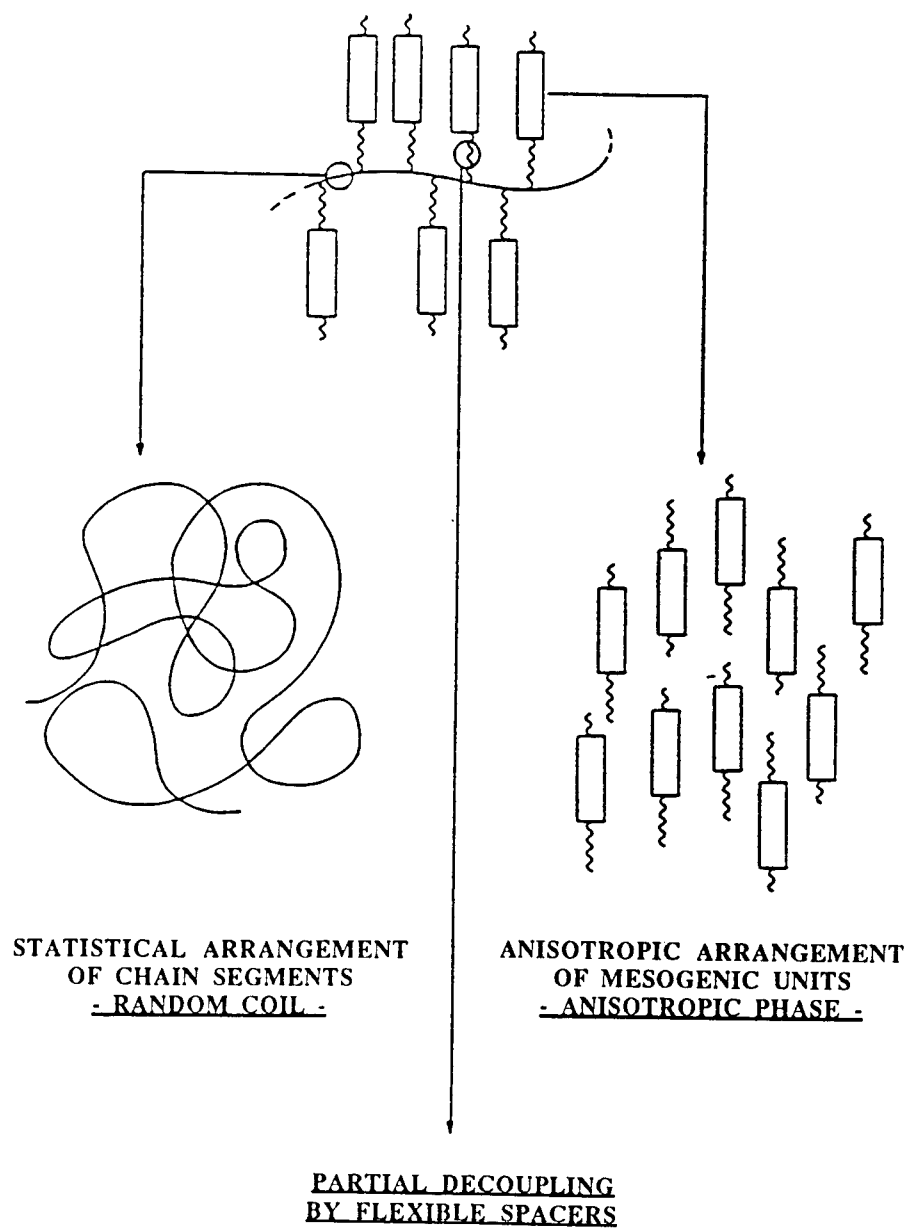
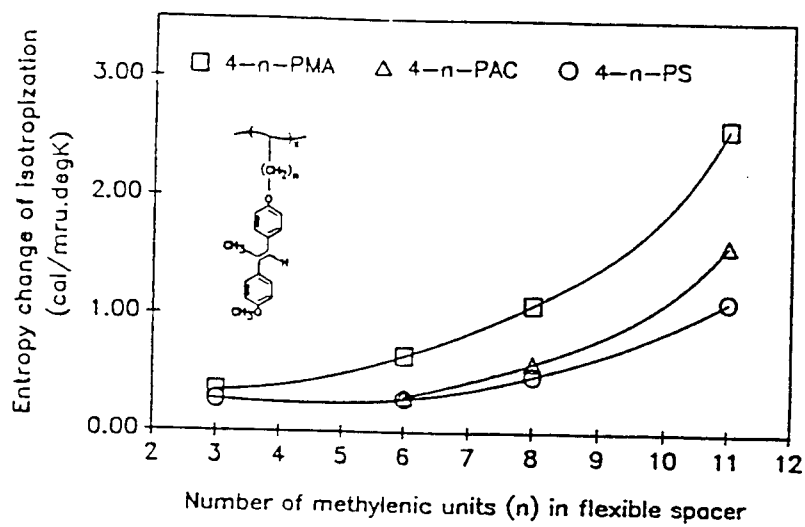


Figure 26

a)



b)

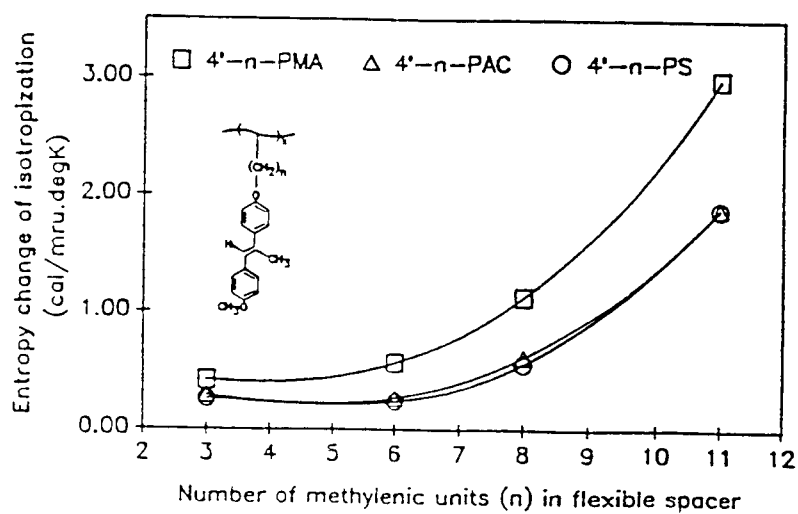
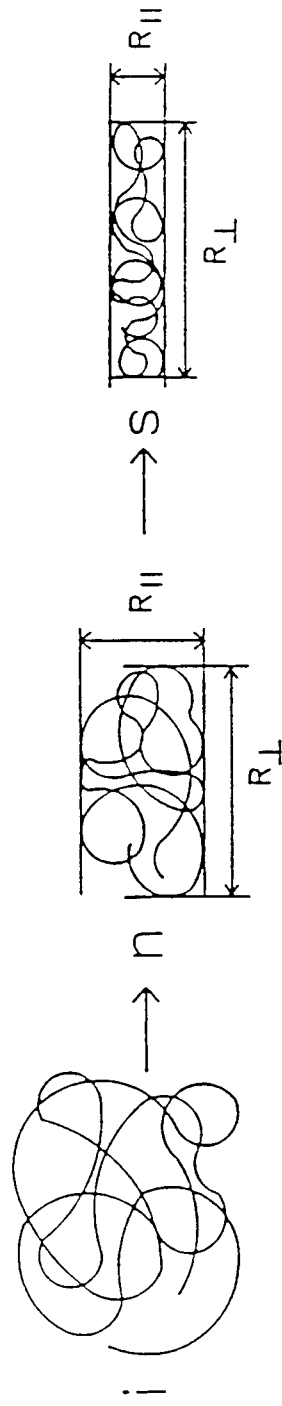


Figure 27

a Theoretical (M. Warner)



b Experimental (Saclay Group)

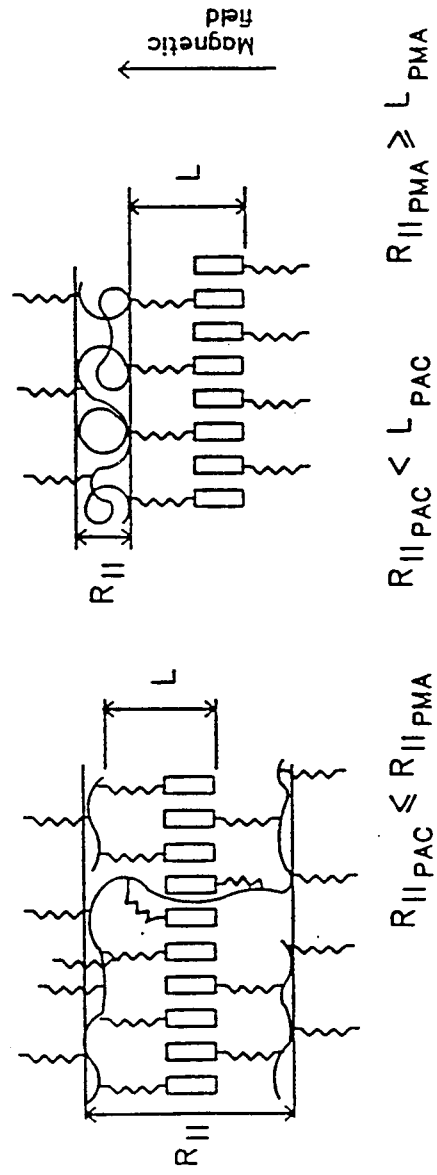


Figure 28

The figure consists of two parts. The top part is a schematic diagram of the polymer structure. It shows two parallel chains of rectangular blocks (representing vinyl alcohol units) connected by wavy lines (representing vinyl acetate units). The distance between the chains is labeled d . The length of the blocks is labeled l . The diagram illustrates the transition from a disordered state to a more ordered state as the temperature decreases.

The bottom part is a graph showing the temperature T_1 in degrees Celsius (°C) on the y-axis versus the distance d in Angstroms (Å) on the x-axis. The y-axis ranges from 30 to 110, and the x-axis ranges from 0 to 1.0. Two curves are plotted: one with open circles and one with closed circles. The open circle curve starts at approximately (0.1, 110) and decreases to (1.0, 30). The closed circle curve starts at approximately (0.1, 30) and increases to (1.0, 110). Arrows indicate the direction of the phase transition: a downward arrow for the open circle curve and an upward arrow for the closed circle curve.

d (Å)	T_1 (°C) (Open Circles)	T_1 (°C) (Closed Circles)
0.1	110	30
0.2	100	35
0.4	85	45
0.6	70	60
0.8	55	80
1.0	30	110

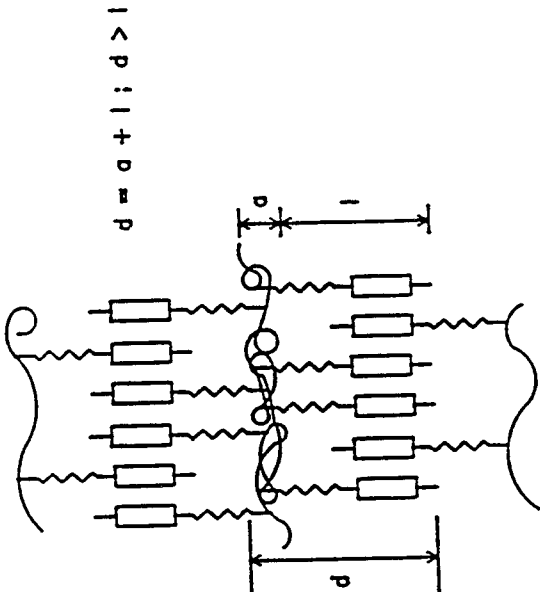
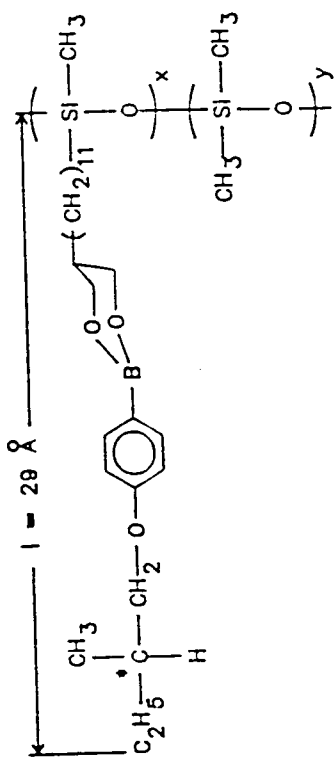


Figure 29

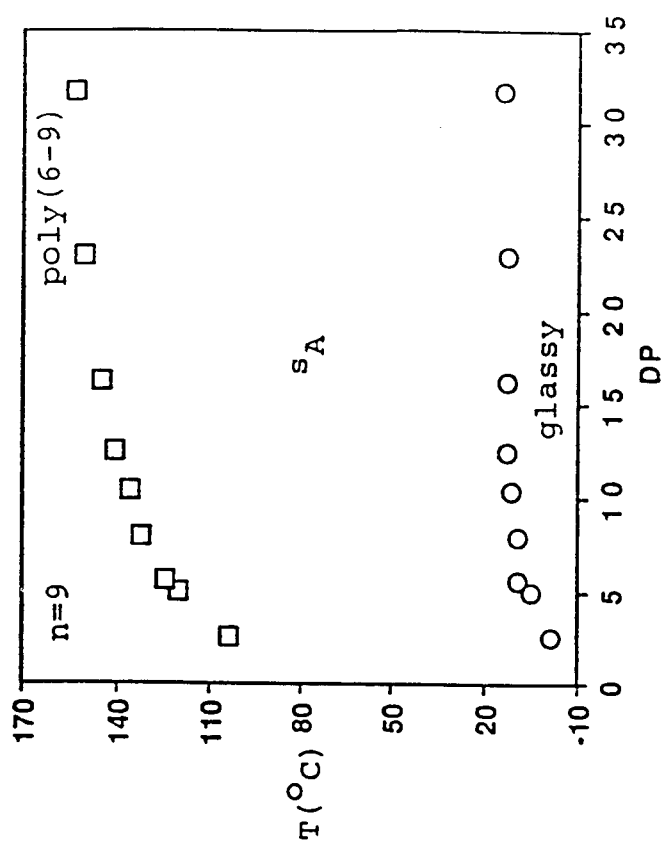
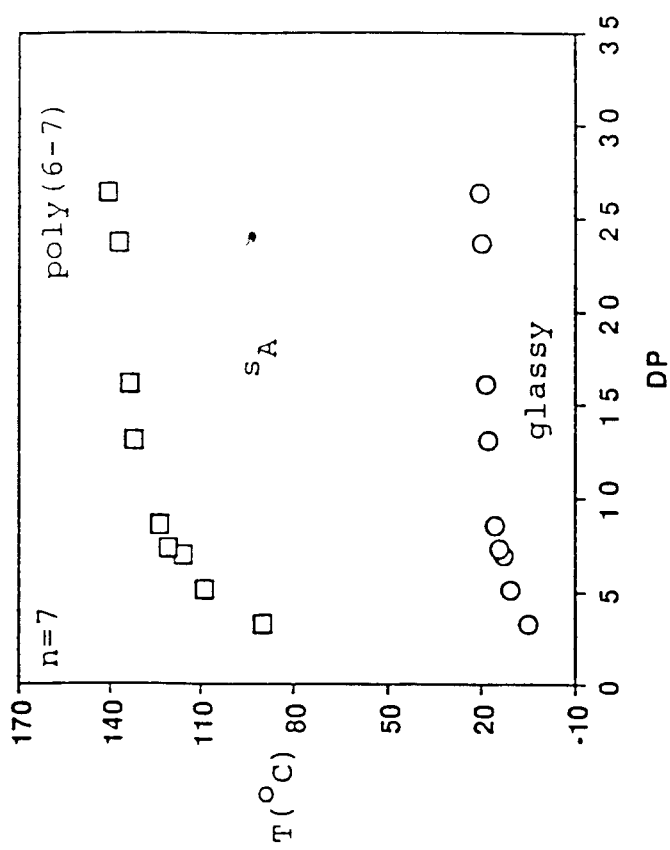
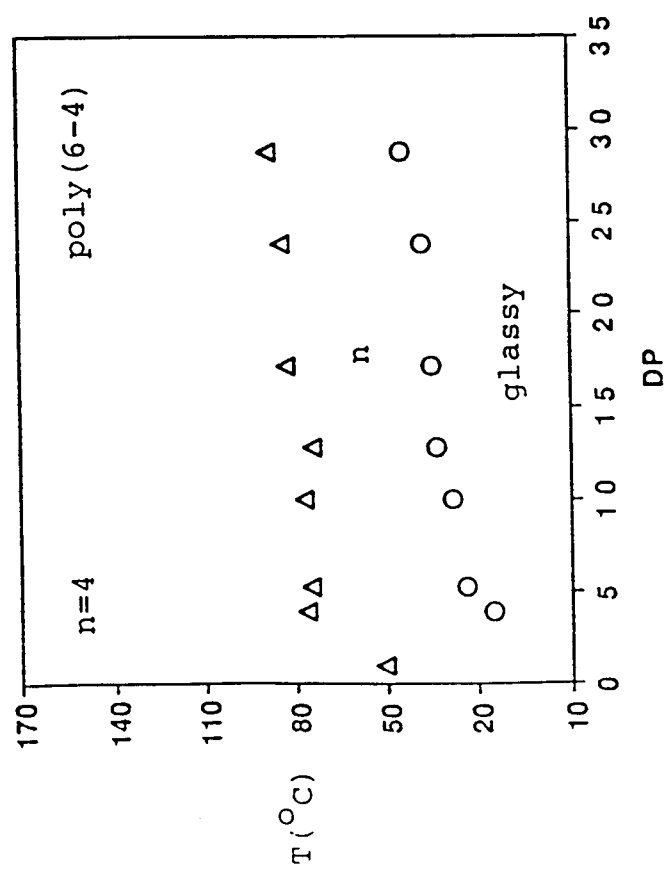
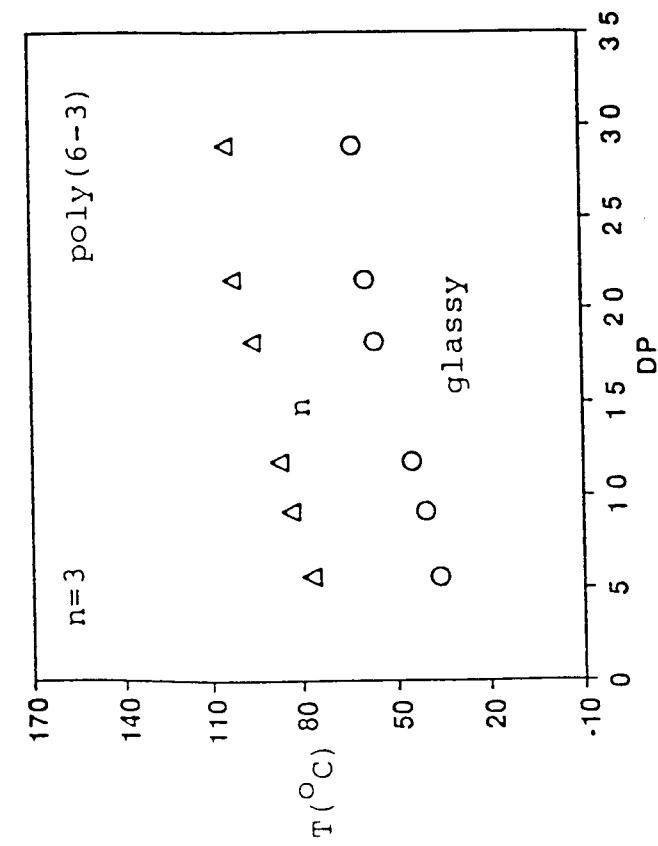


Figure 30

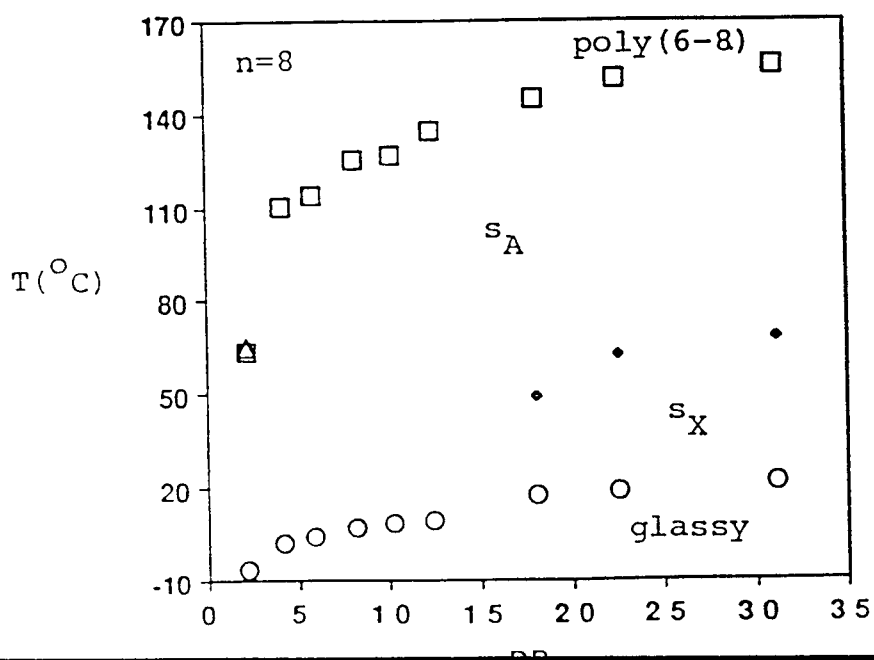
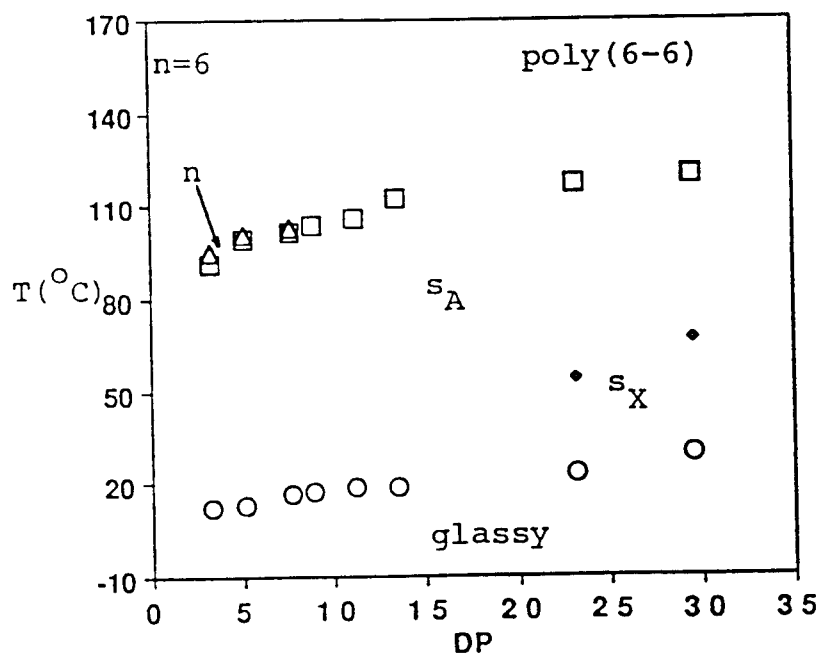
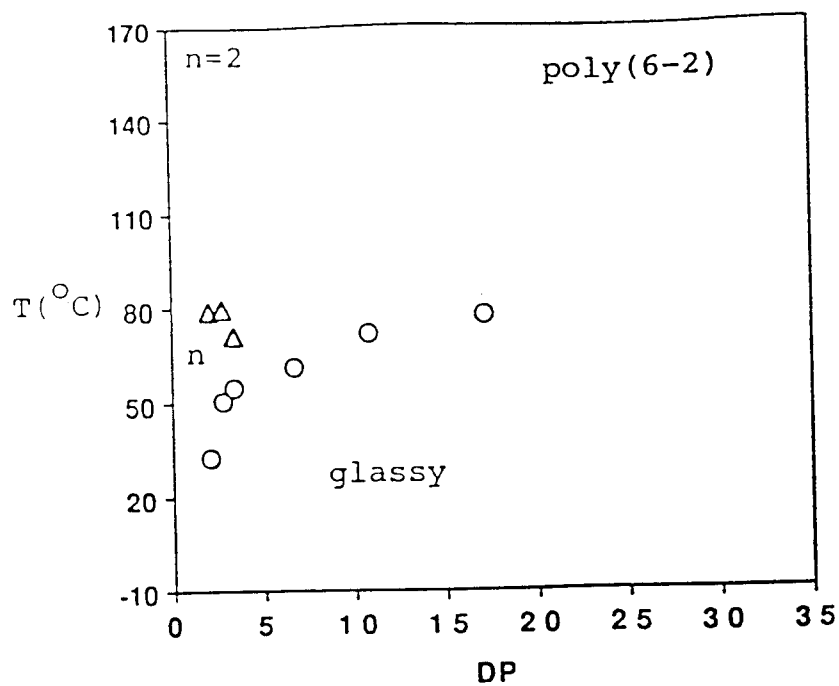


Figure 31

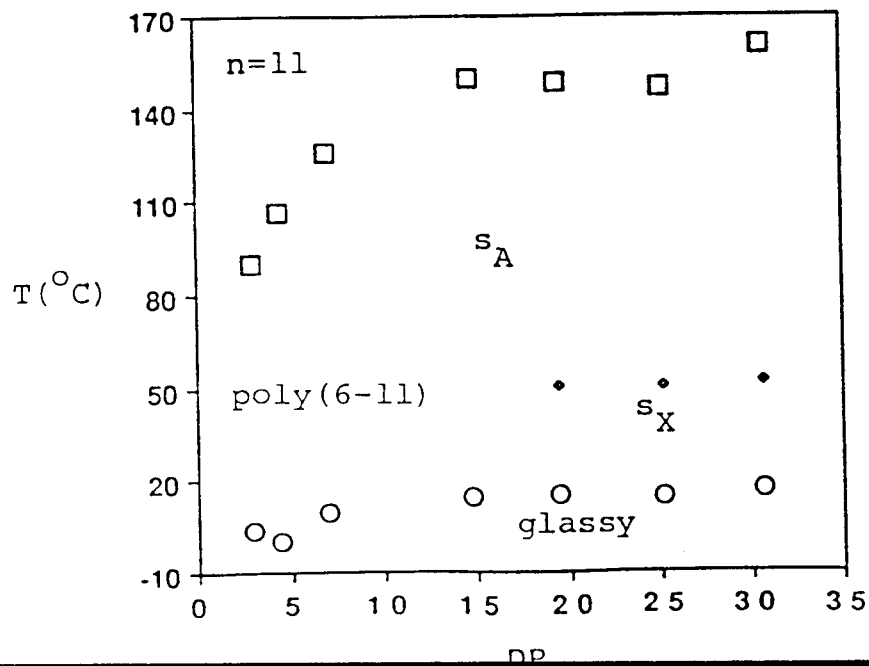
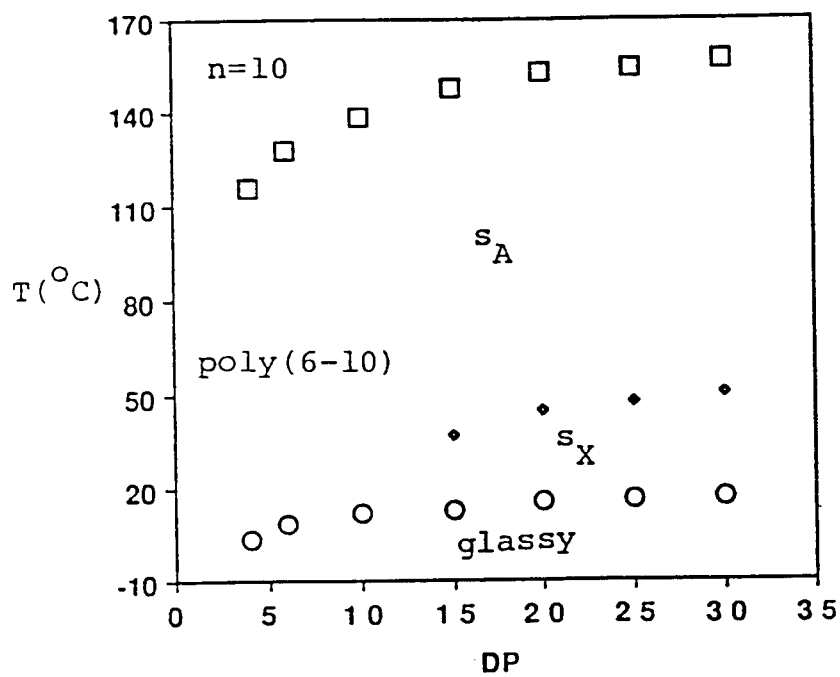
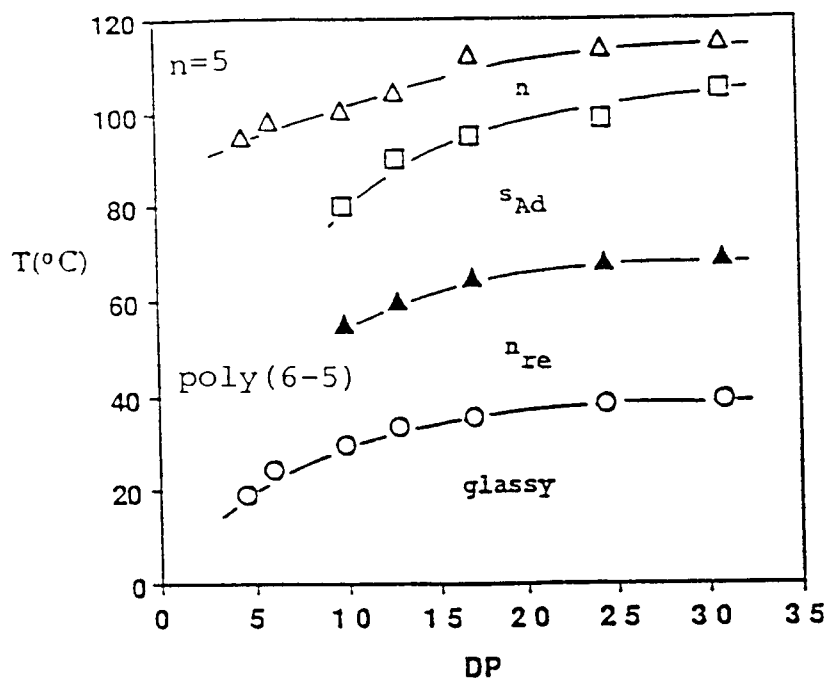


Figure 32

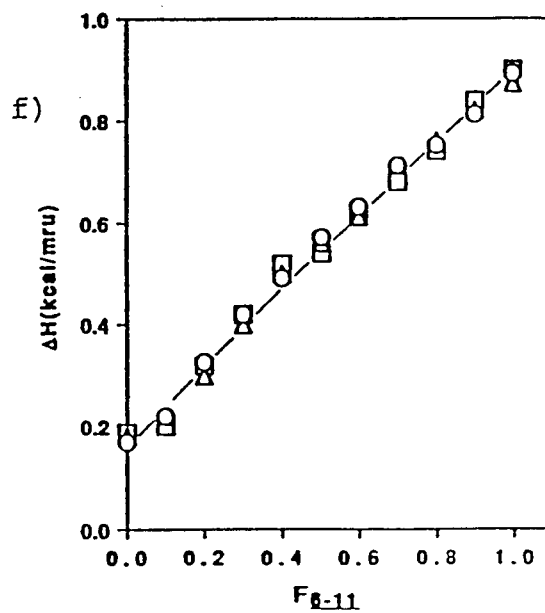
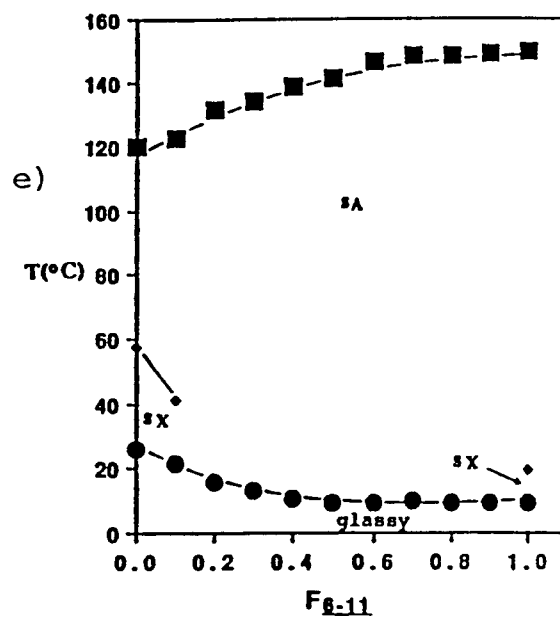
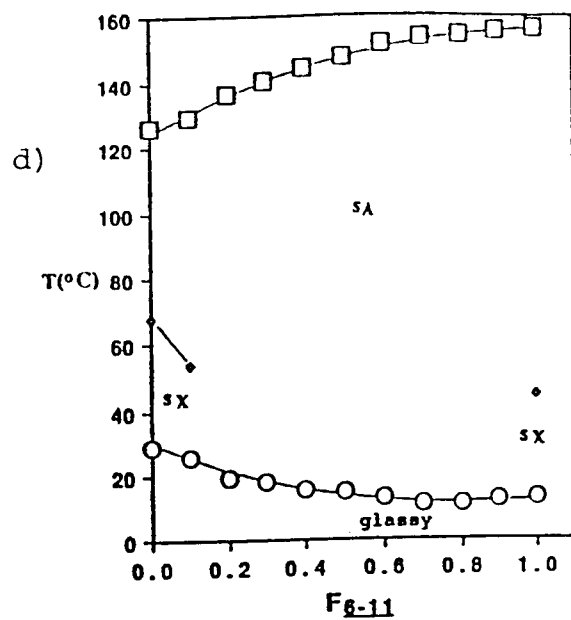
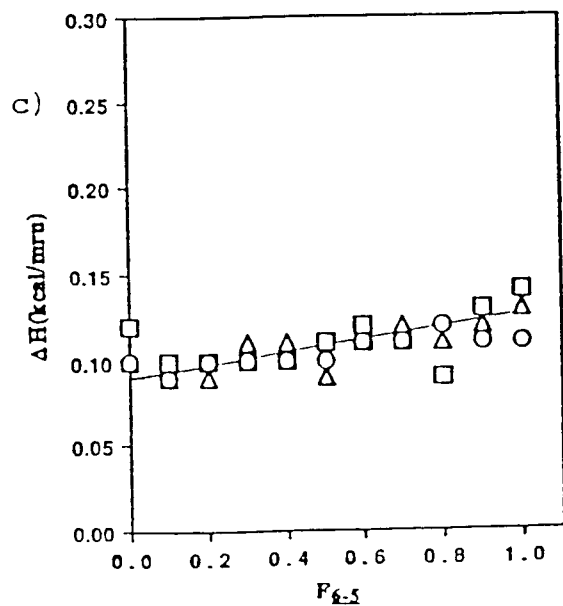
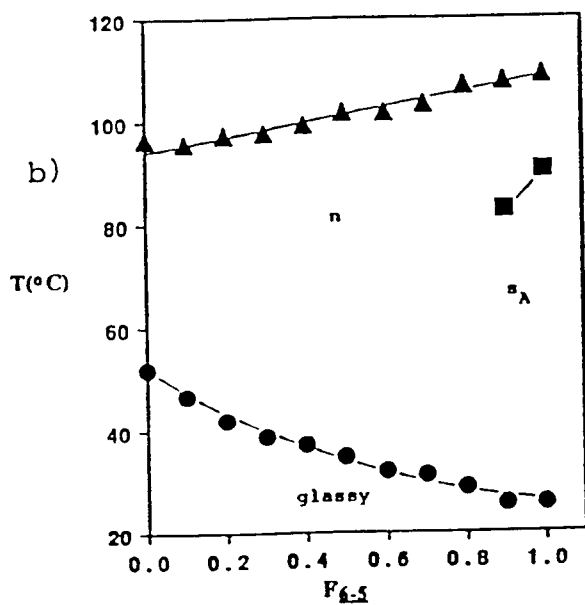
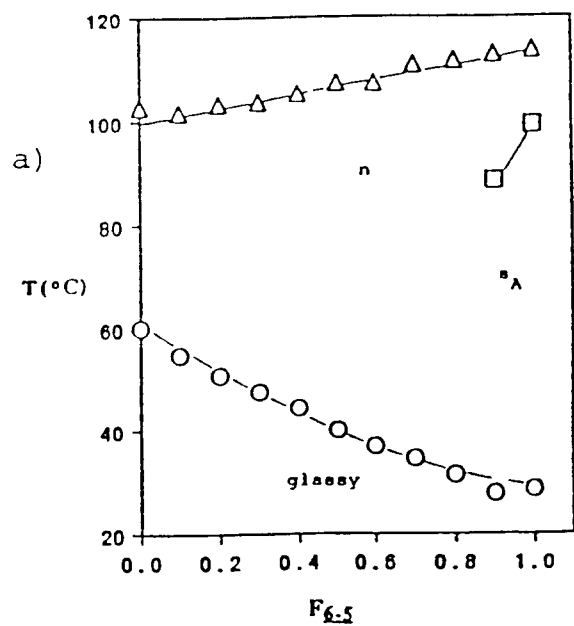
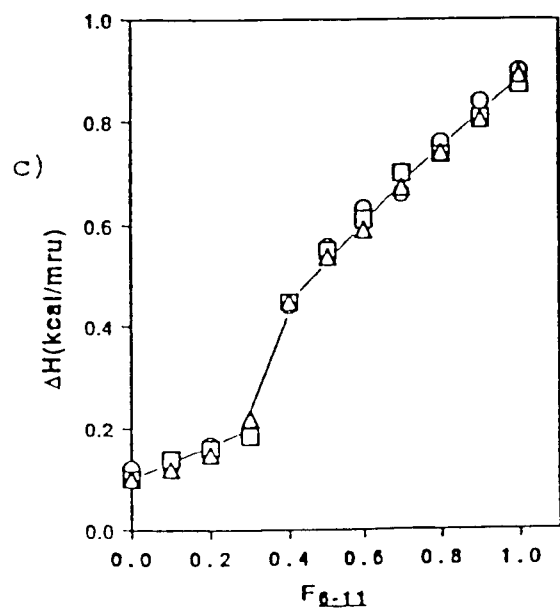
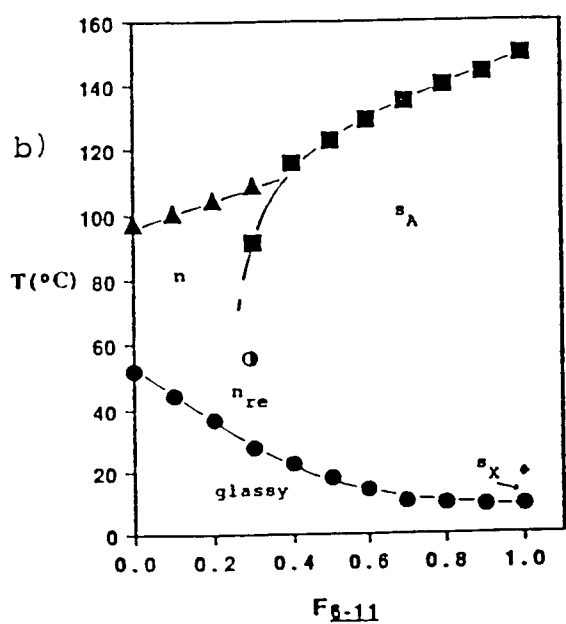
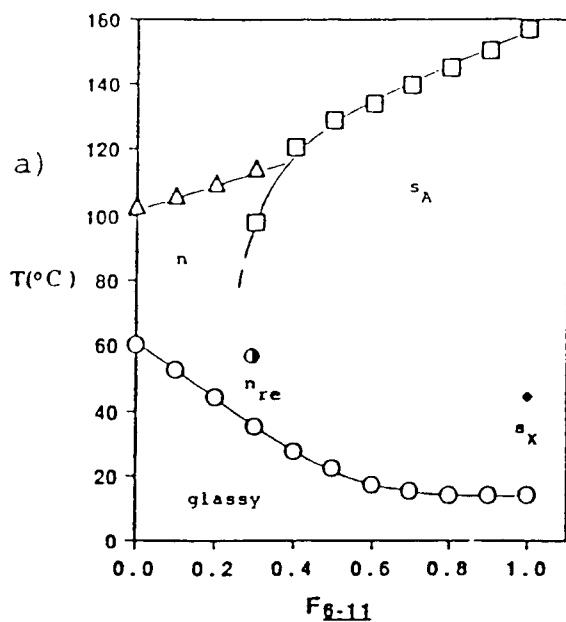


Figure 33

Poly[(6-3)-co-(6-11)]X/Y (DP=20)



Poly[(6-5)-co-(6-11)]X/Y (DP=20)

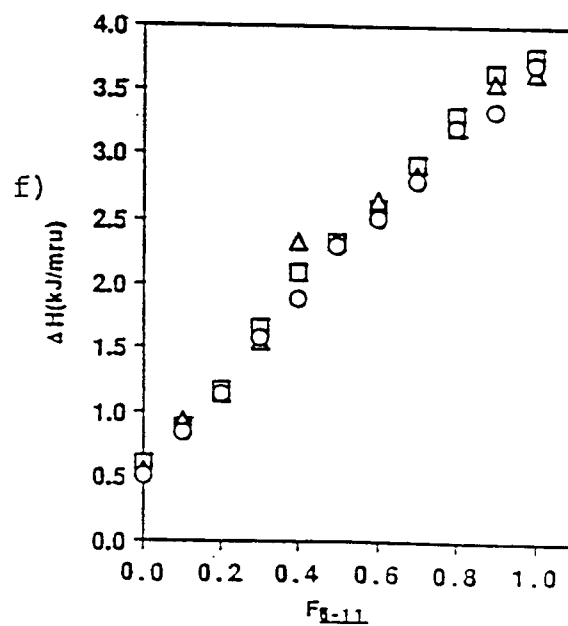
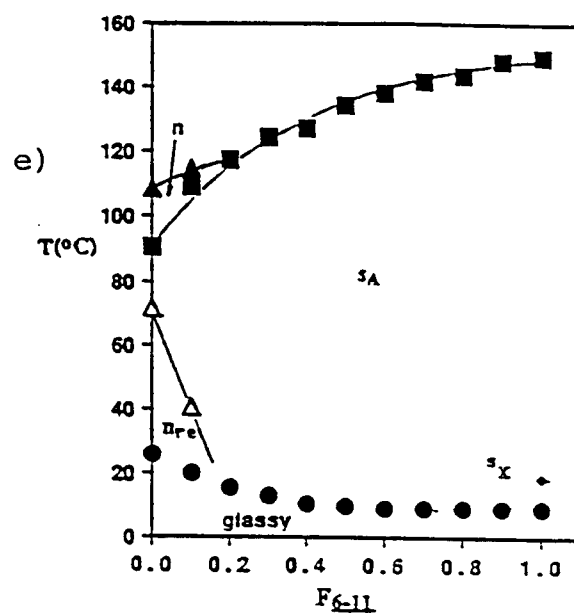
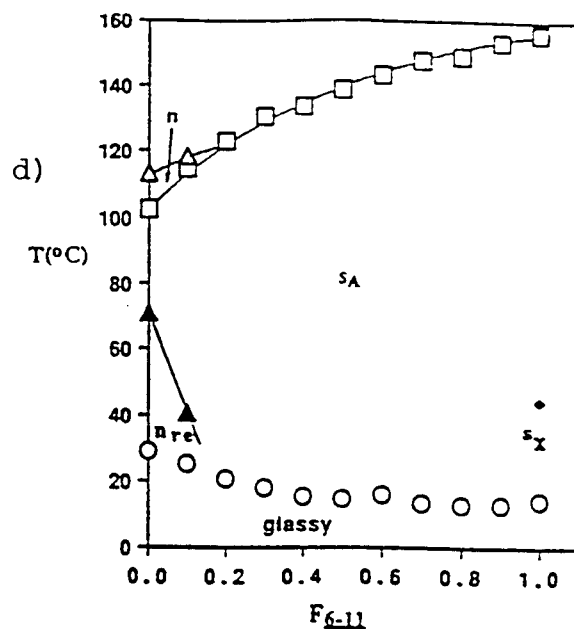


Figure 34

Poly[(6-2)-co-(6-8)]X/Y (DP=10)

Poly[(6-2)-co-(6-11)]X/Y (DP=15)

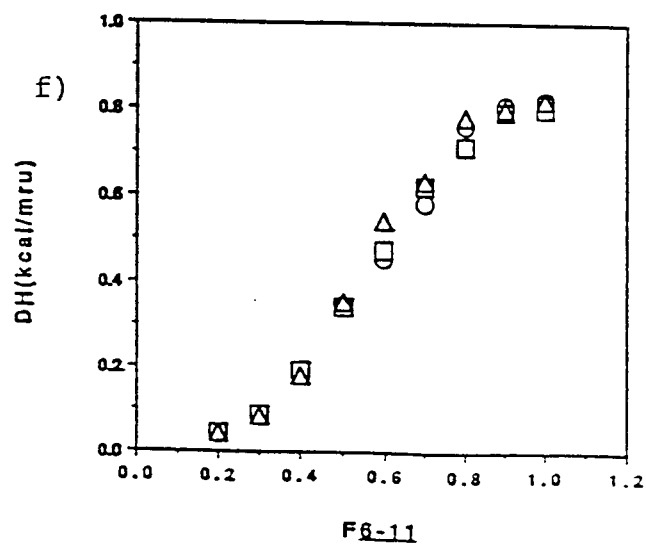
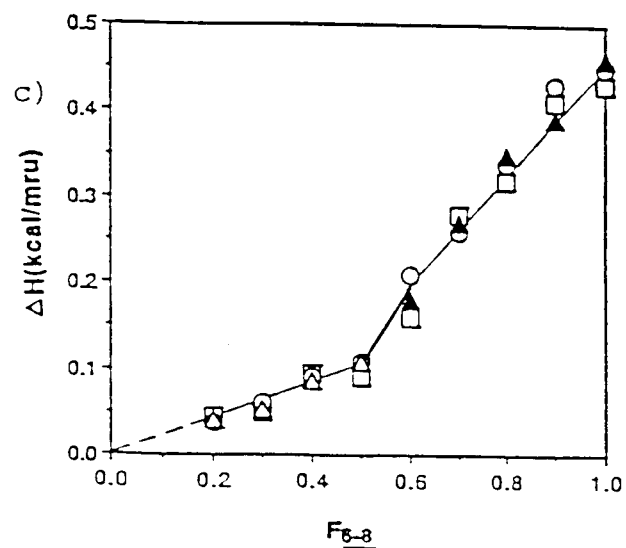
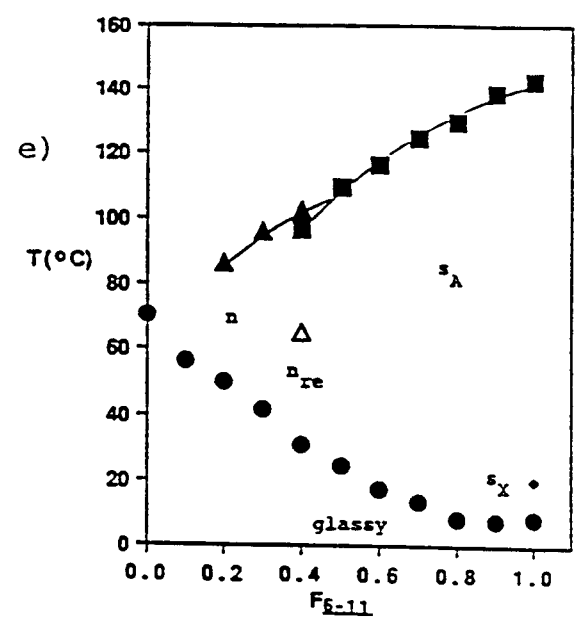
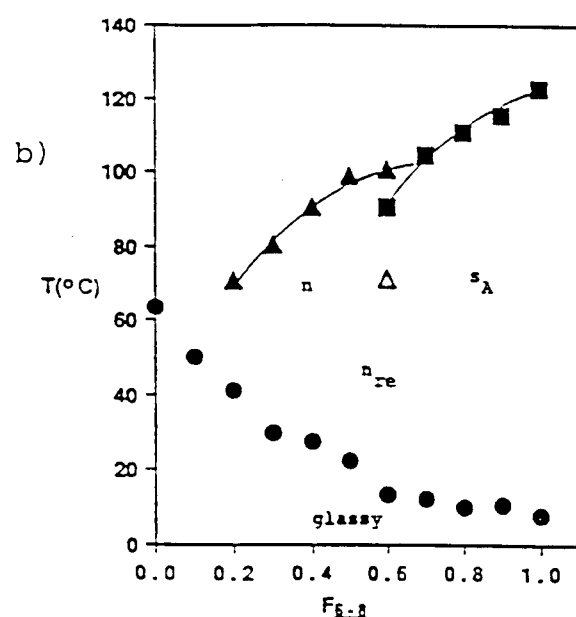
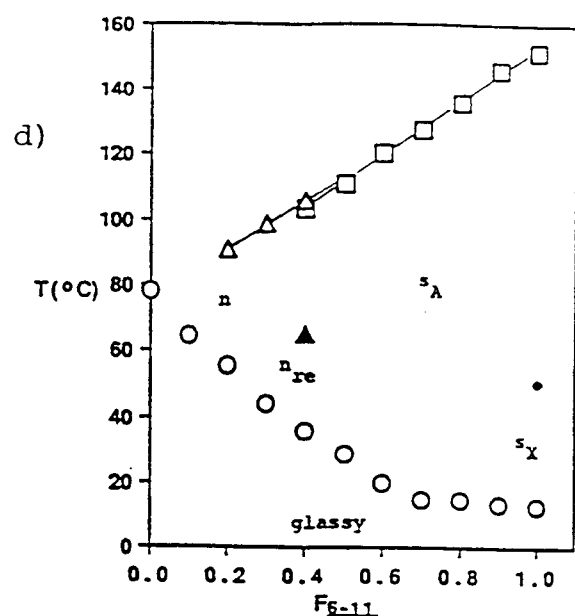
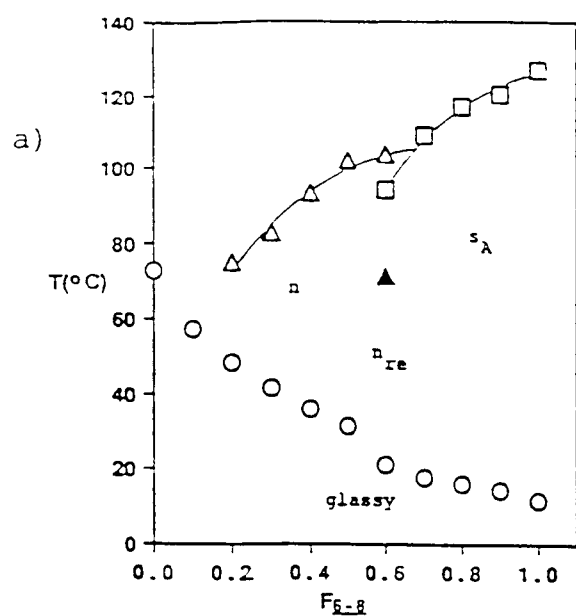


Figure 35

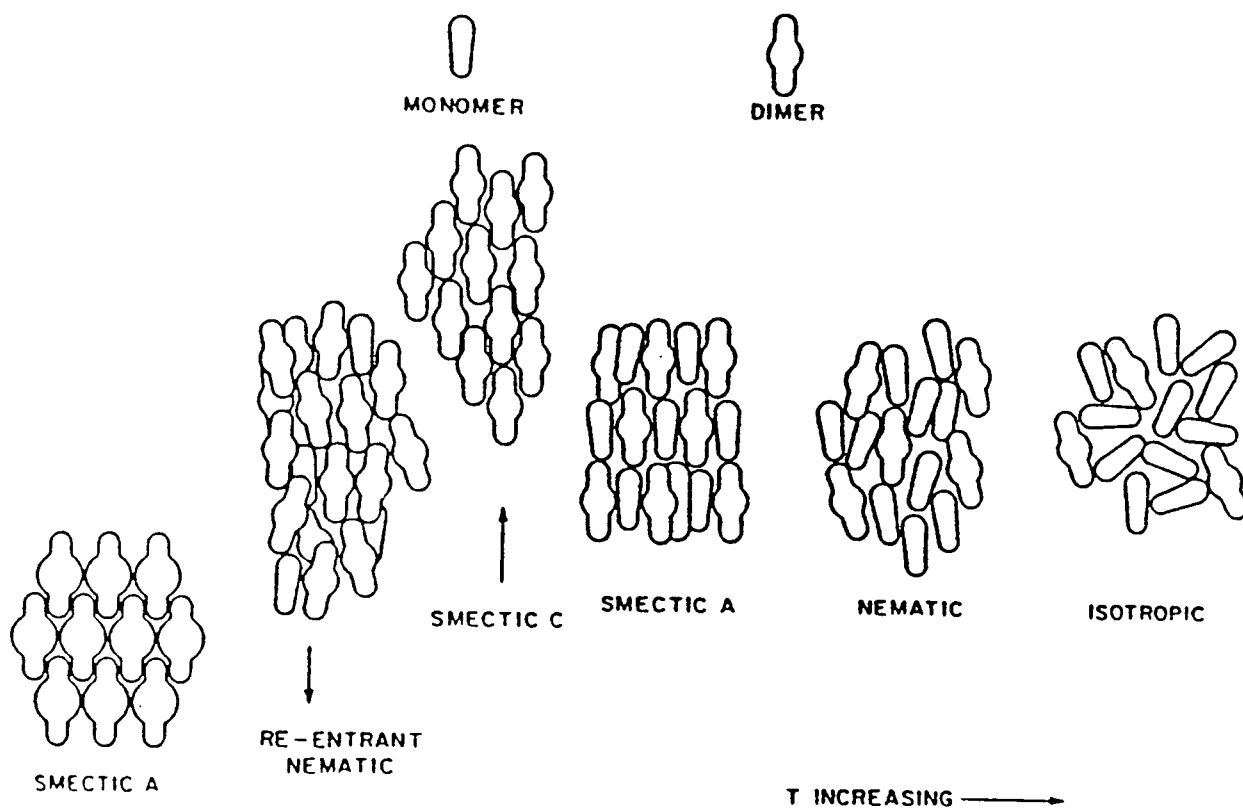


Figure 36

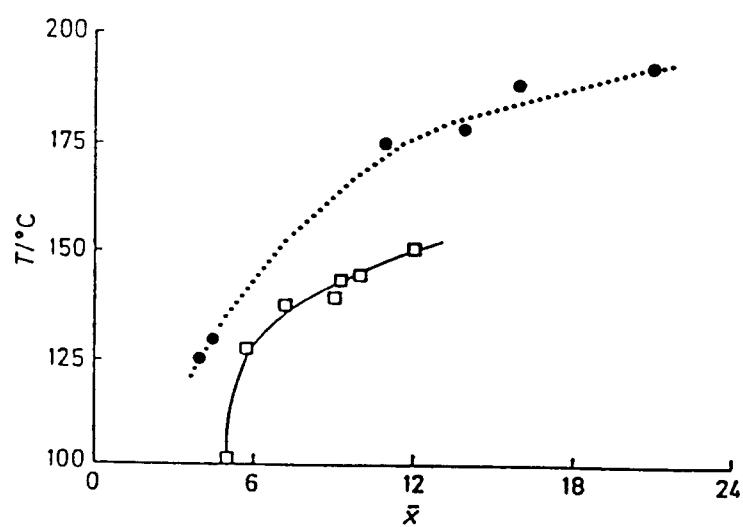
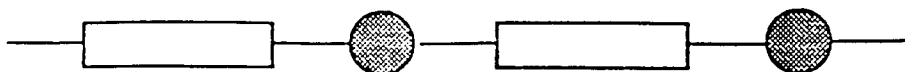


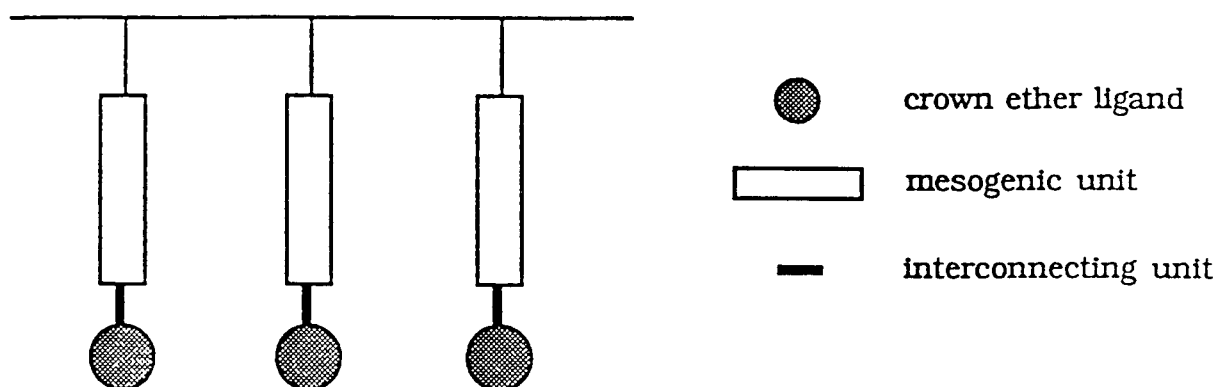
Figure 37

I. Main Chain Liquid Crystalline Polymers



II. Side Chain Liquid Crystalline Polymers

A. Crown ether ligand as part of the mesogenic unit



B. Crown ether ligand as part of the polymer backbone

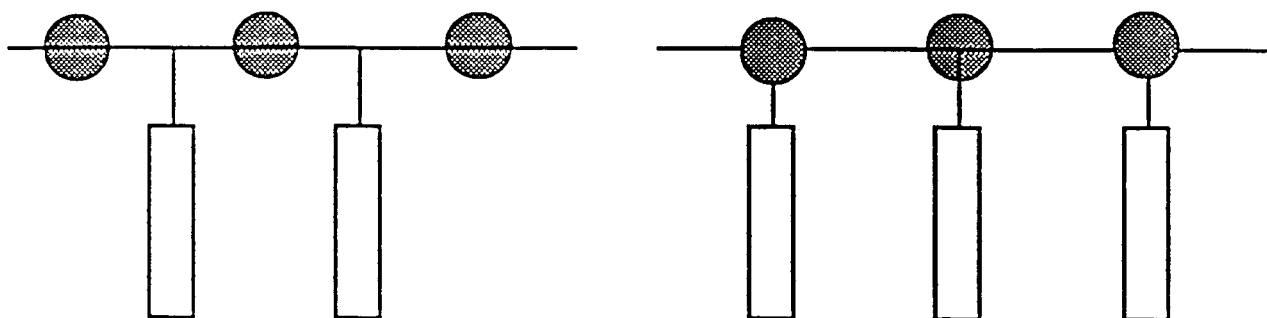


Figure 38

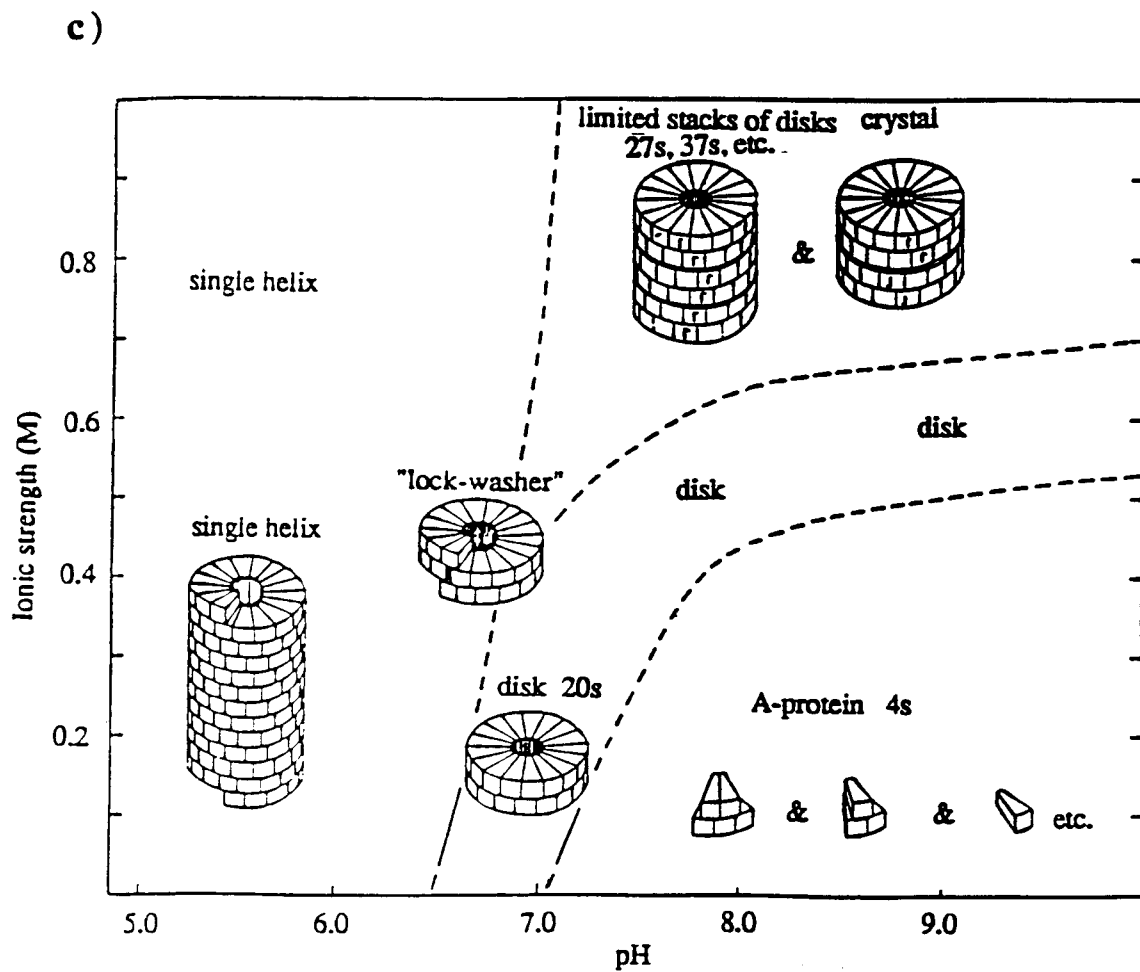
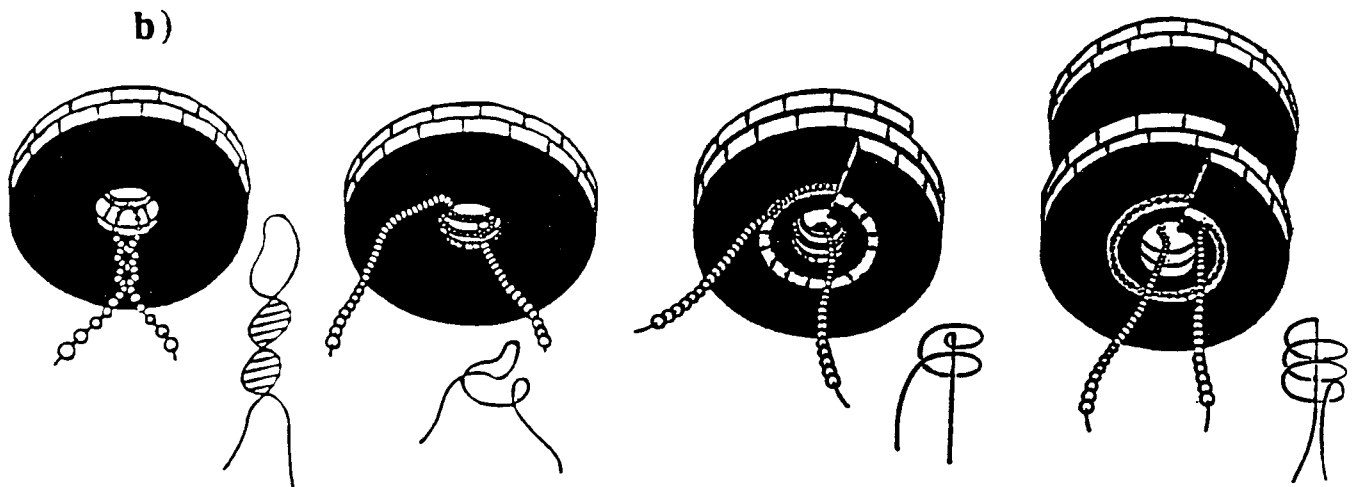
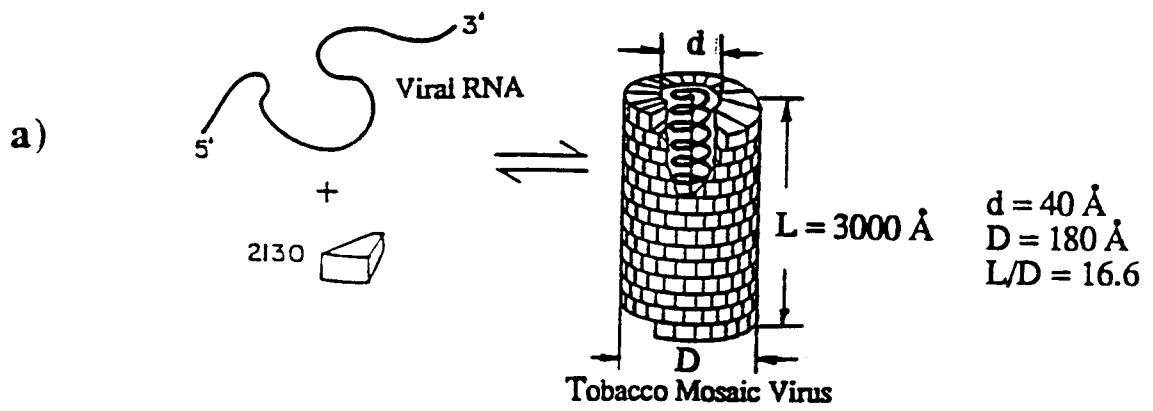


Figure 39

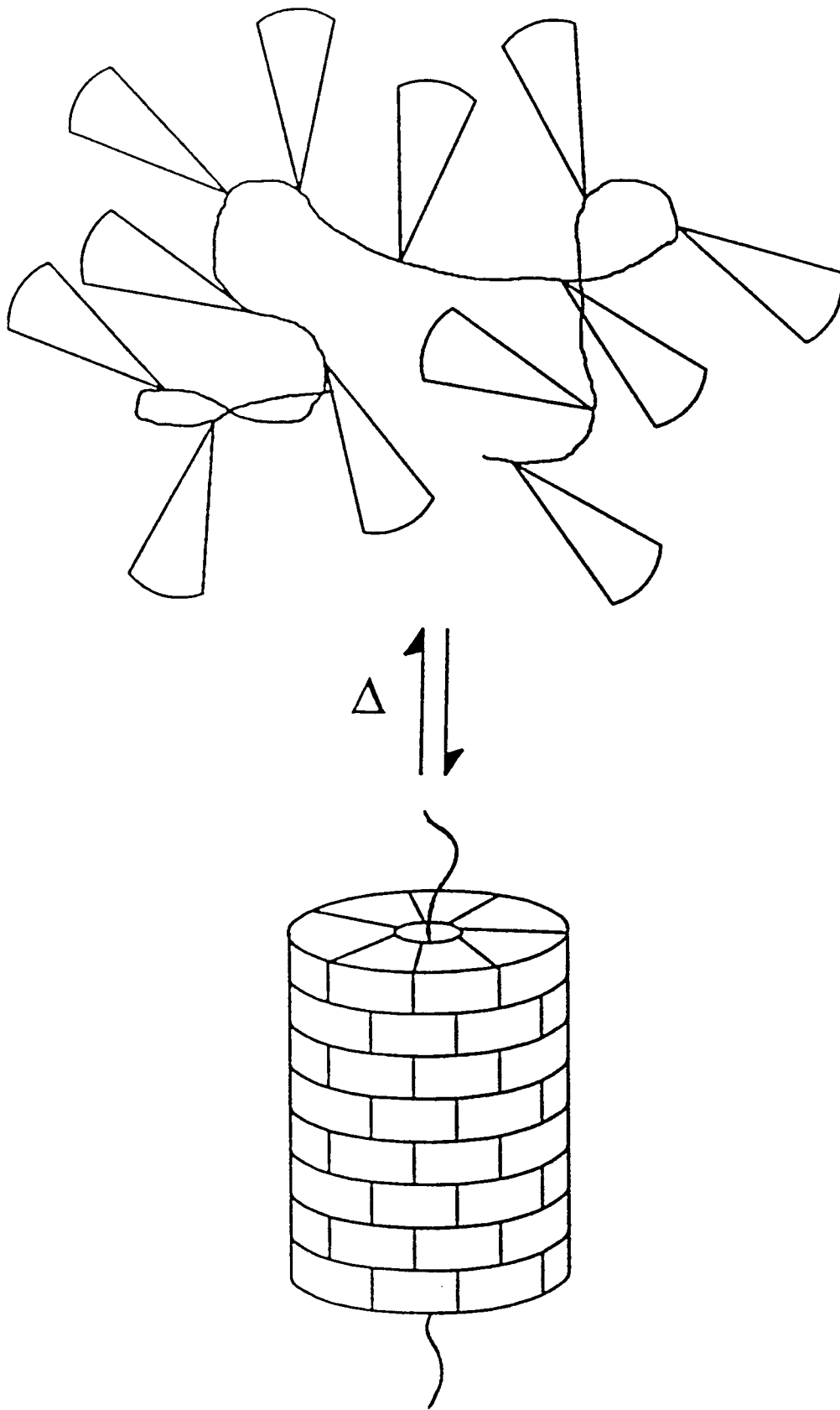
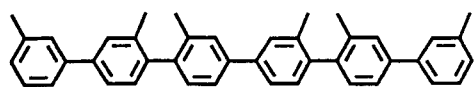
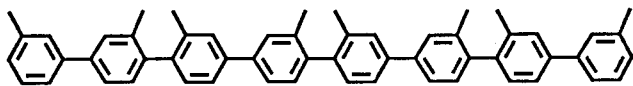


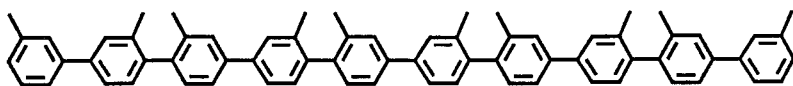
Figure 40



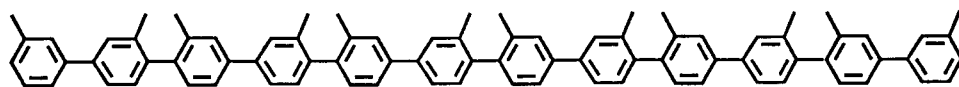
k 142 °C i



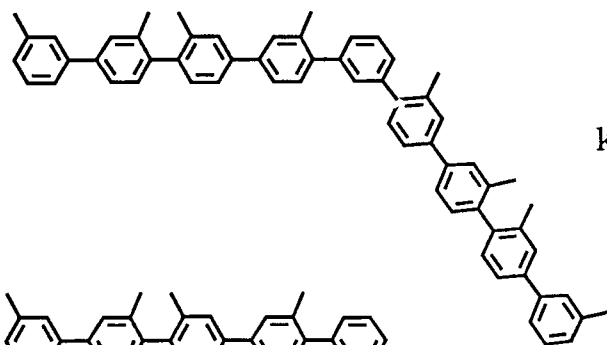
k 273 °C n 311 °C i



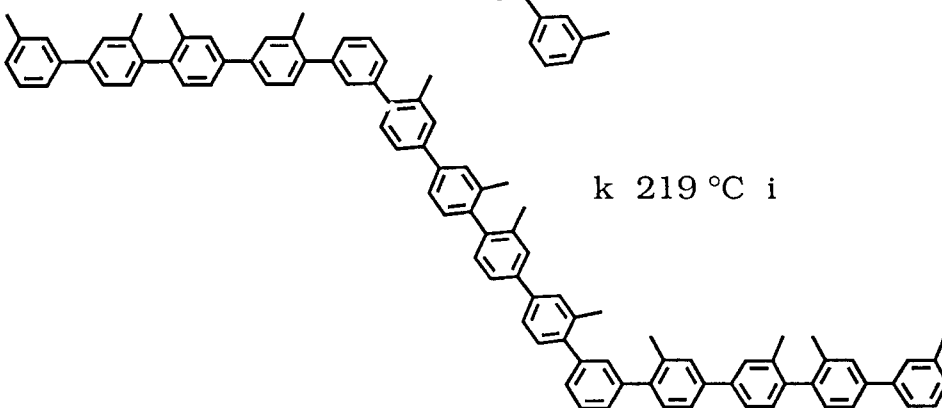
k 242 °C s 260 °C n →



k 298 °C n → > 500 °C

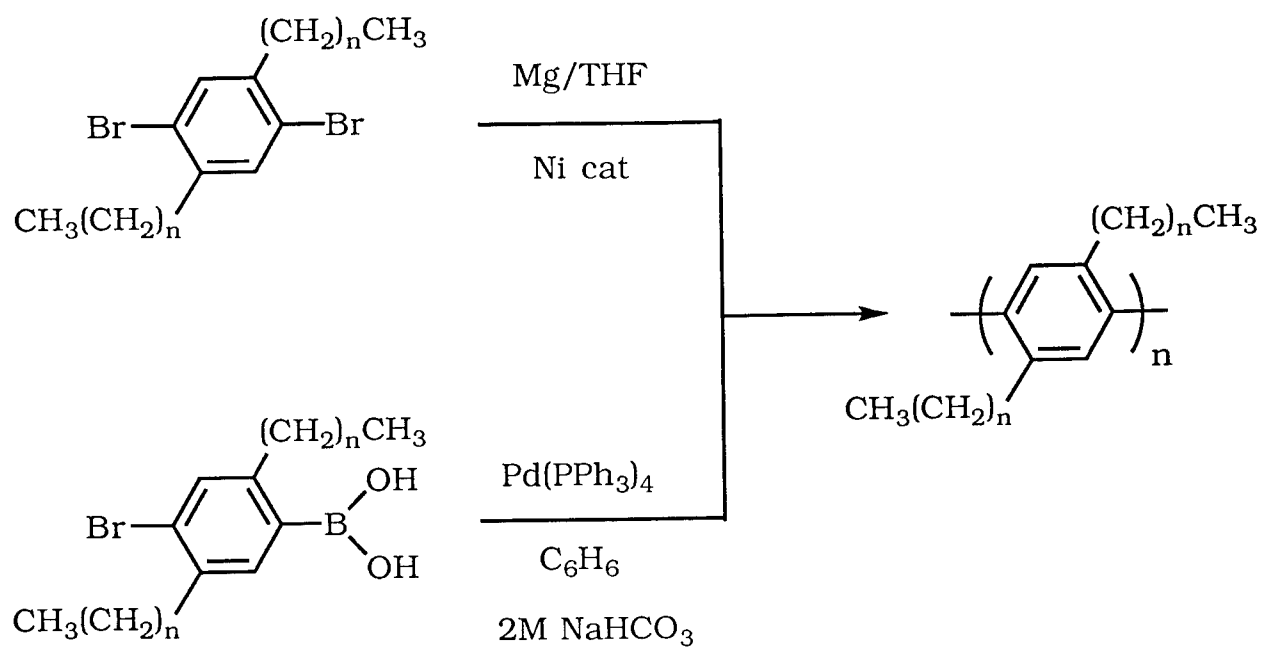


k 171 °C i

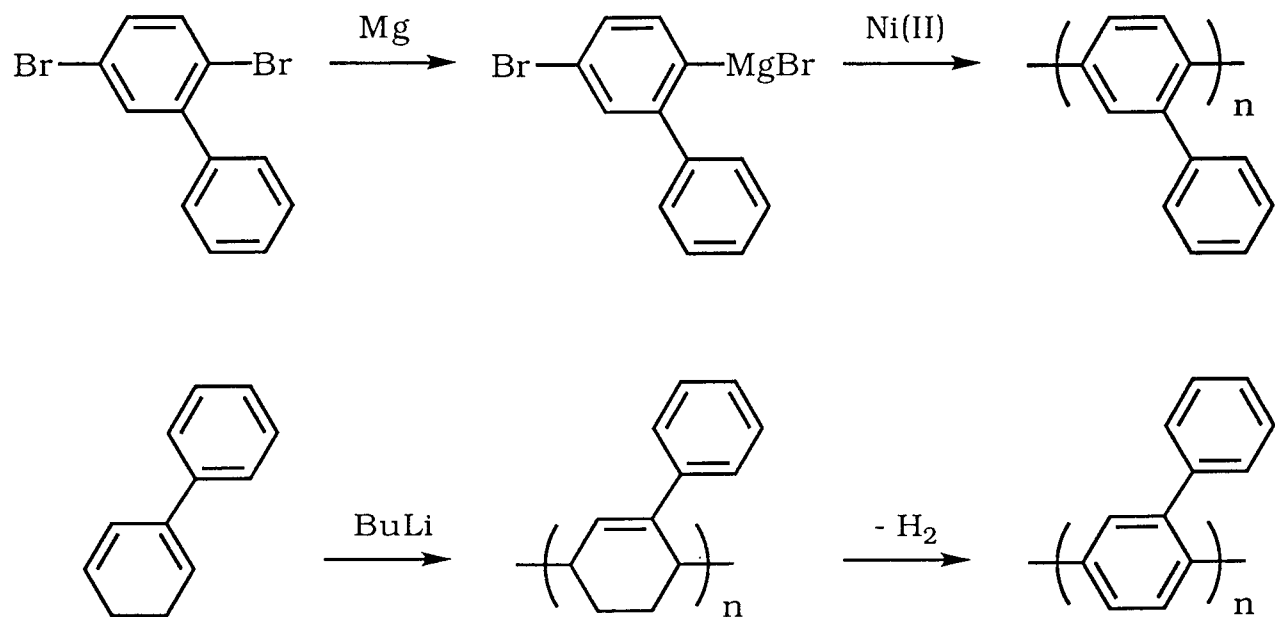


k 219 °C i

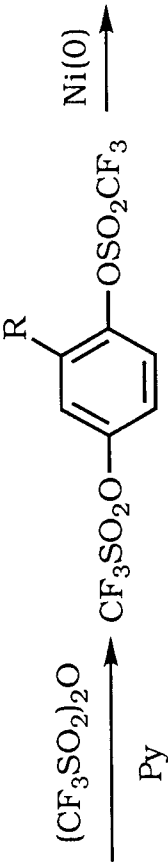
Scheme 1



Scheme 2

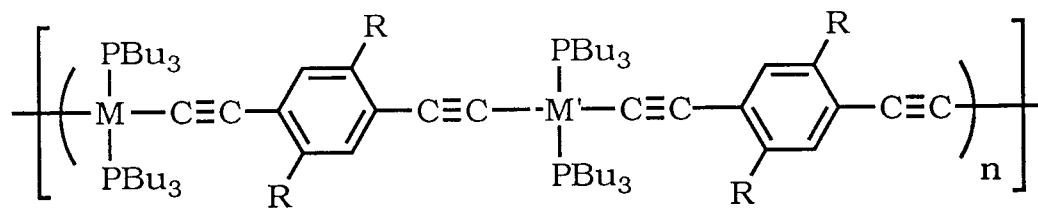
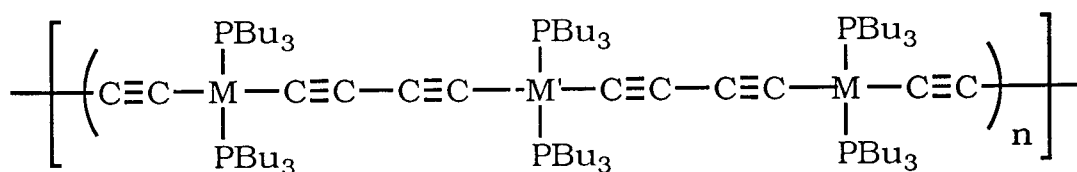
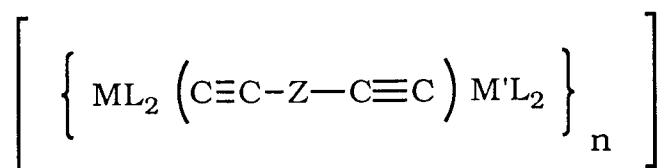
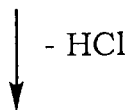
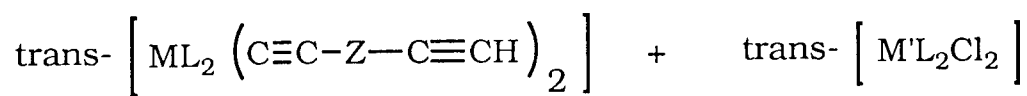


Scheme 3

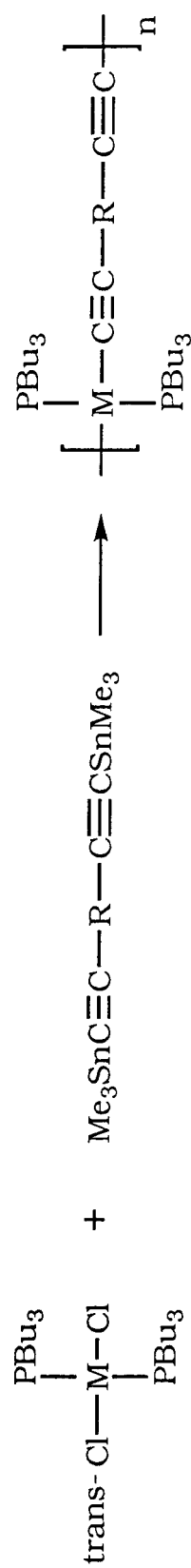


R = Ph, t-Bu, -COOC₂H₅ etc.

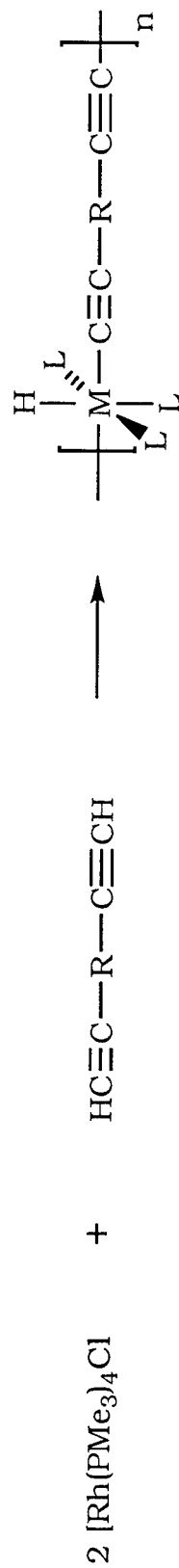
Scheme 4



Scheme 5

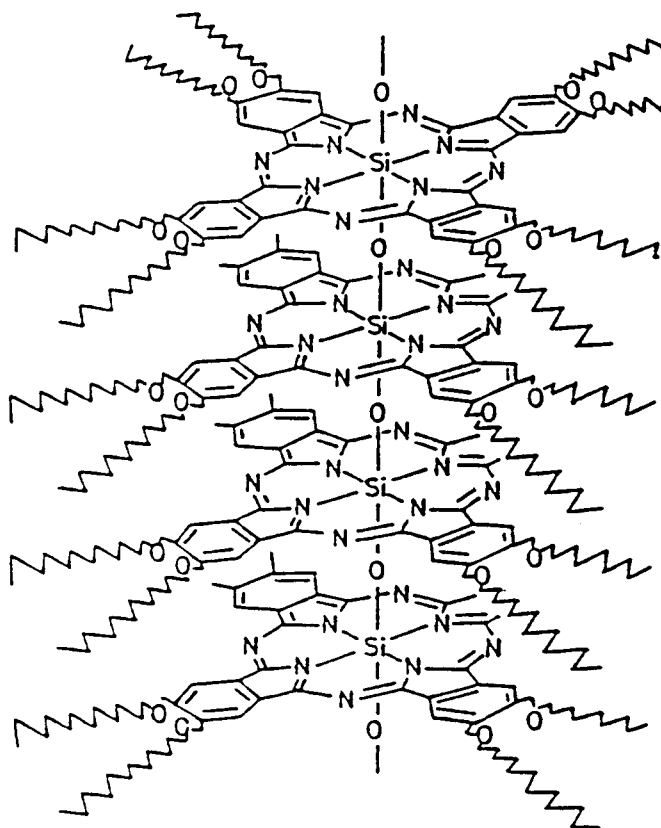
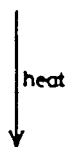
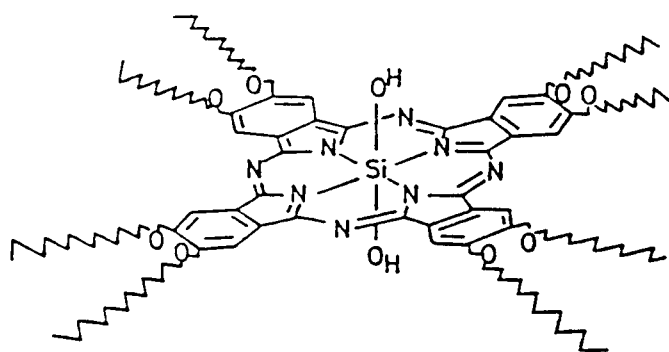


M = Ni, Pd, Pt

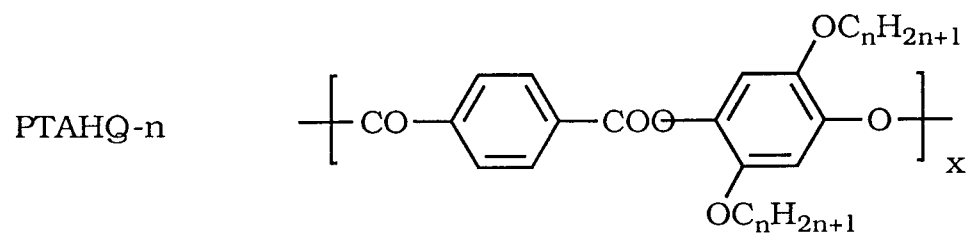
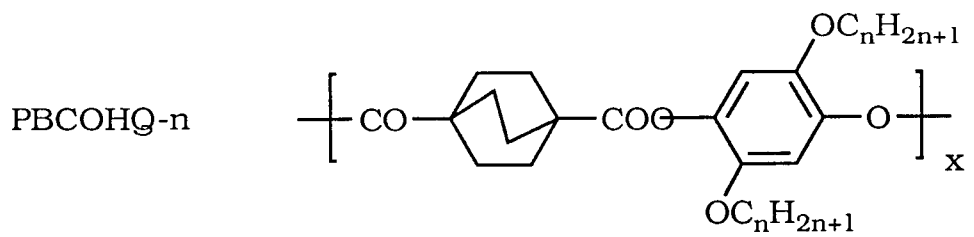
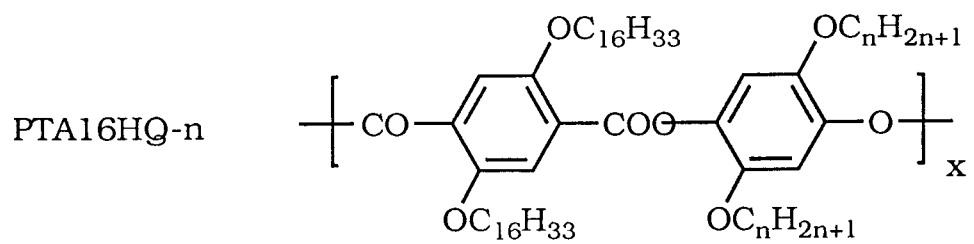


R = p-C₆H₄ etc.

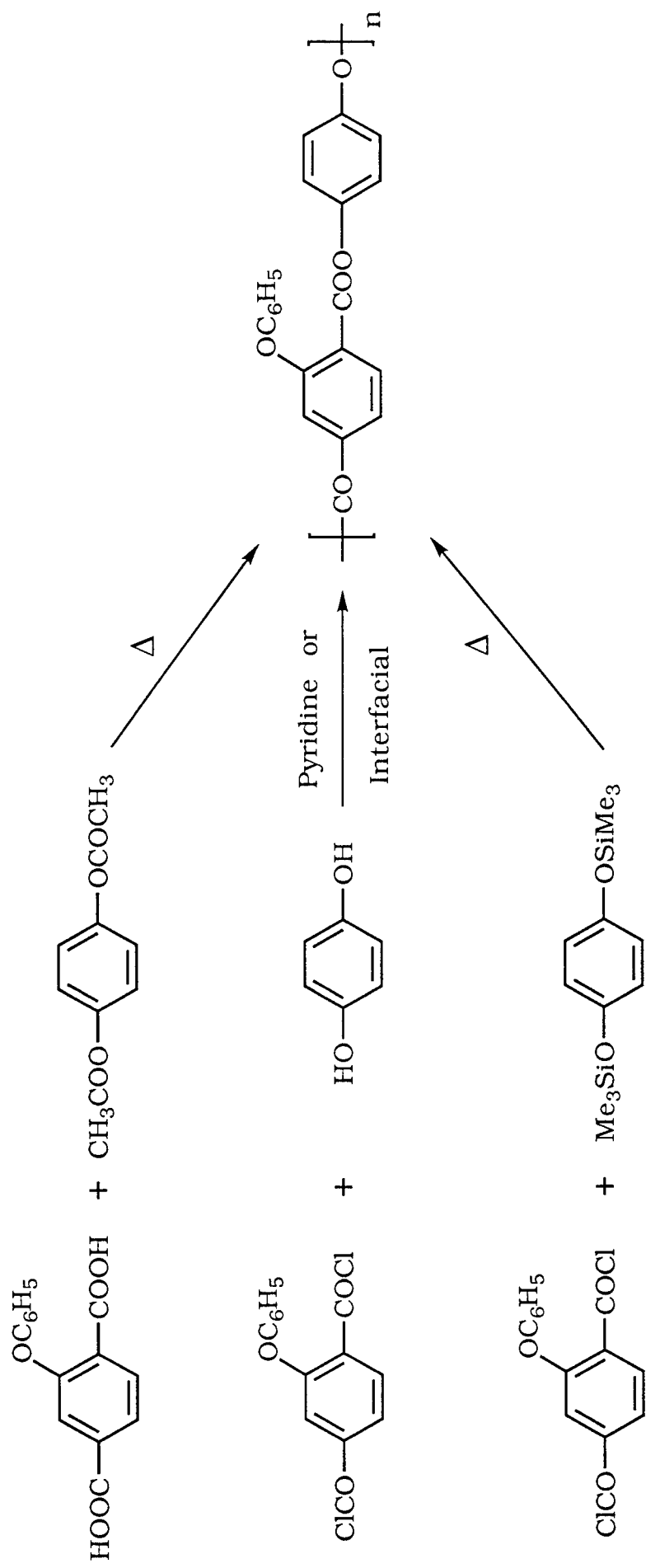
Scheme 6



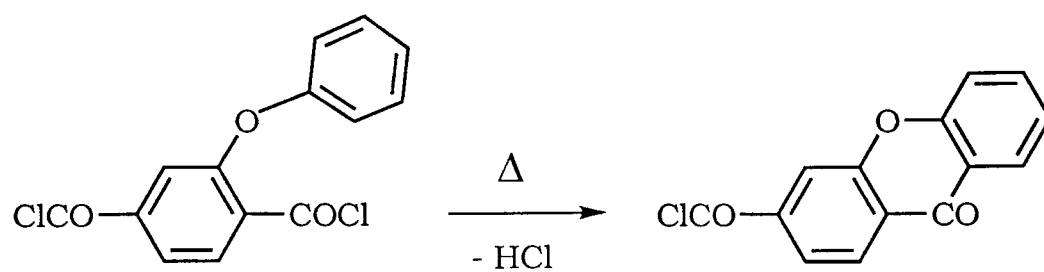
Scheme 7



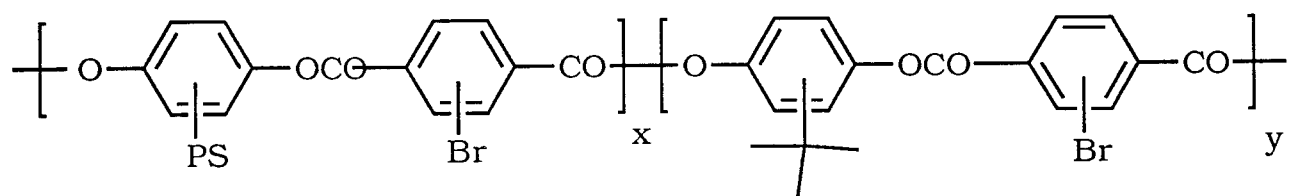
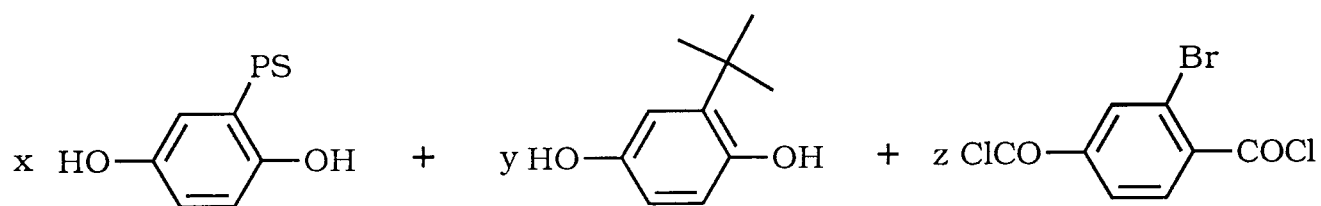
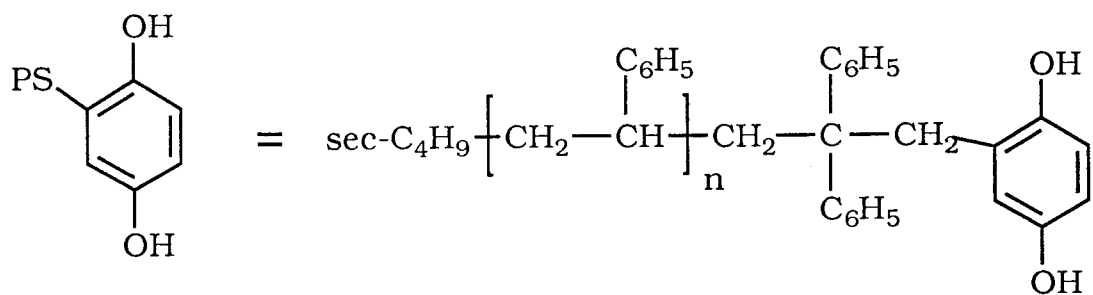
Scheme 8



Scheme 9

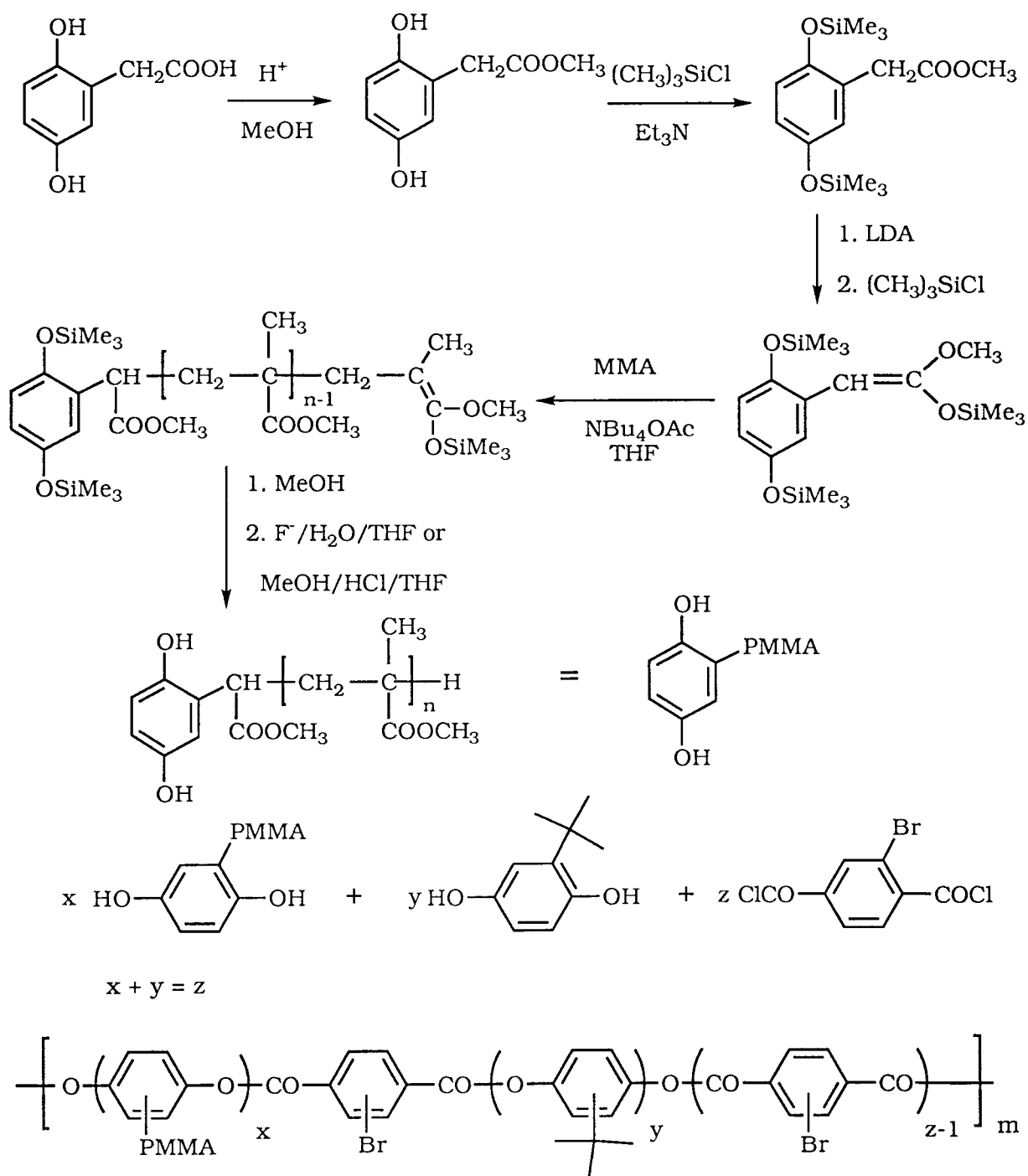


Scheme 10

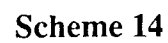


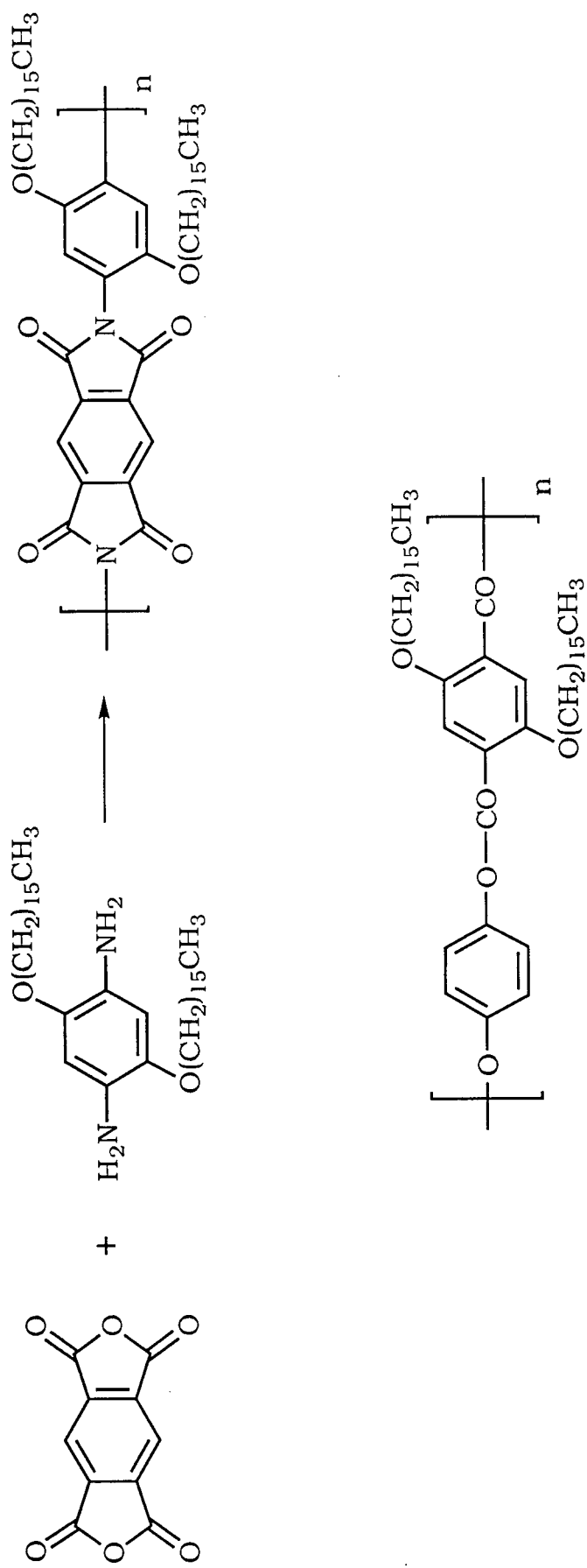
$$x + y = z$$

Scheme 11

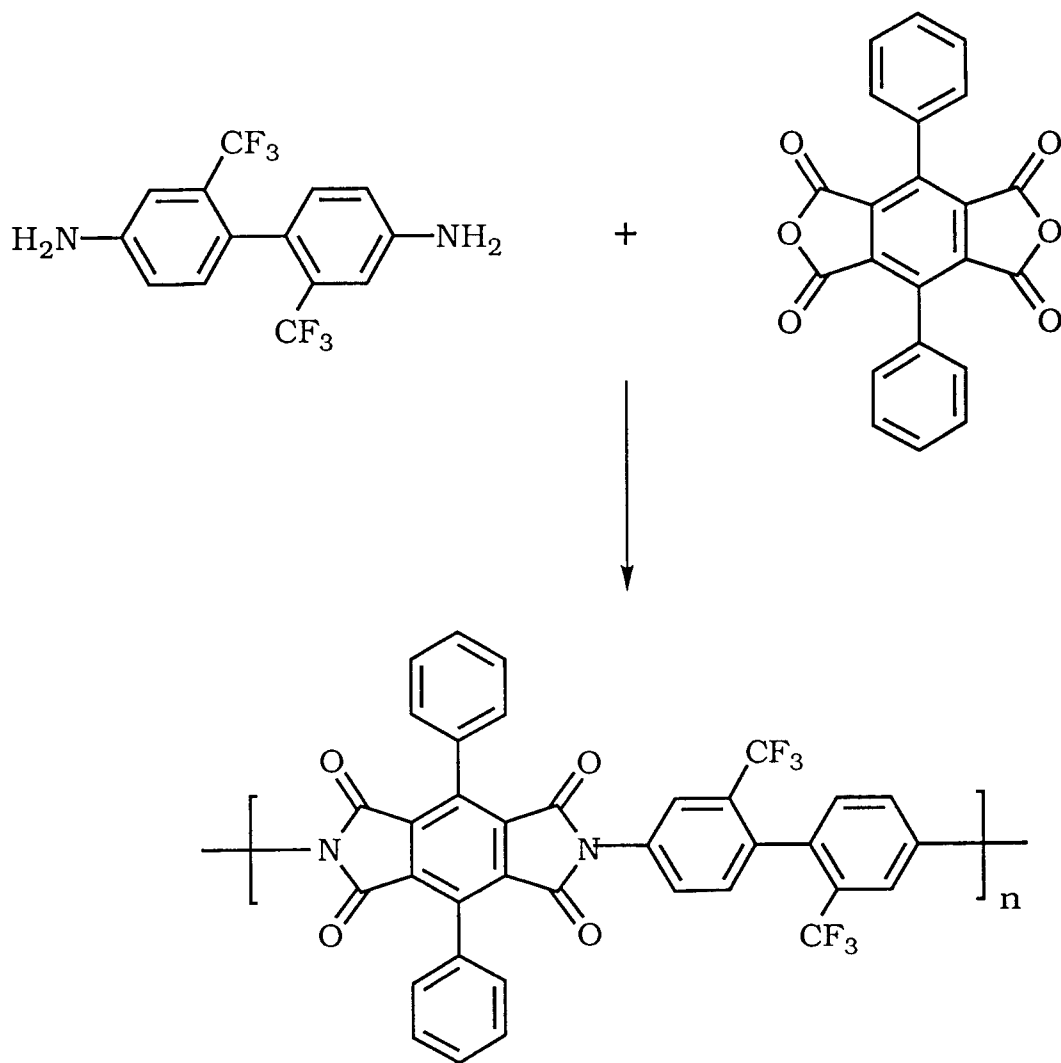


Scheme 12

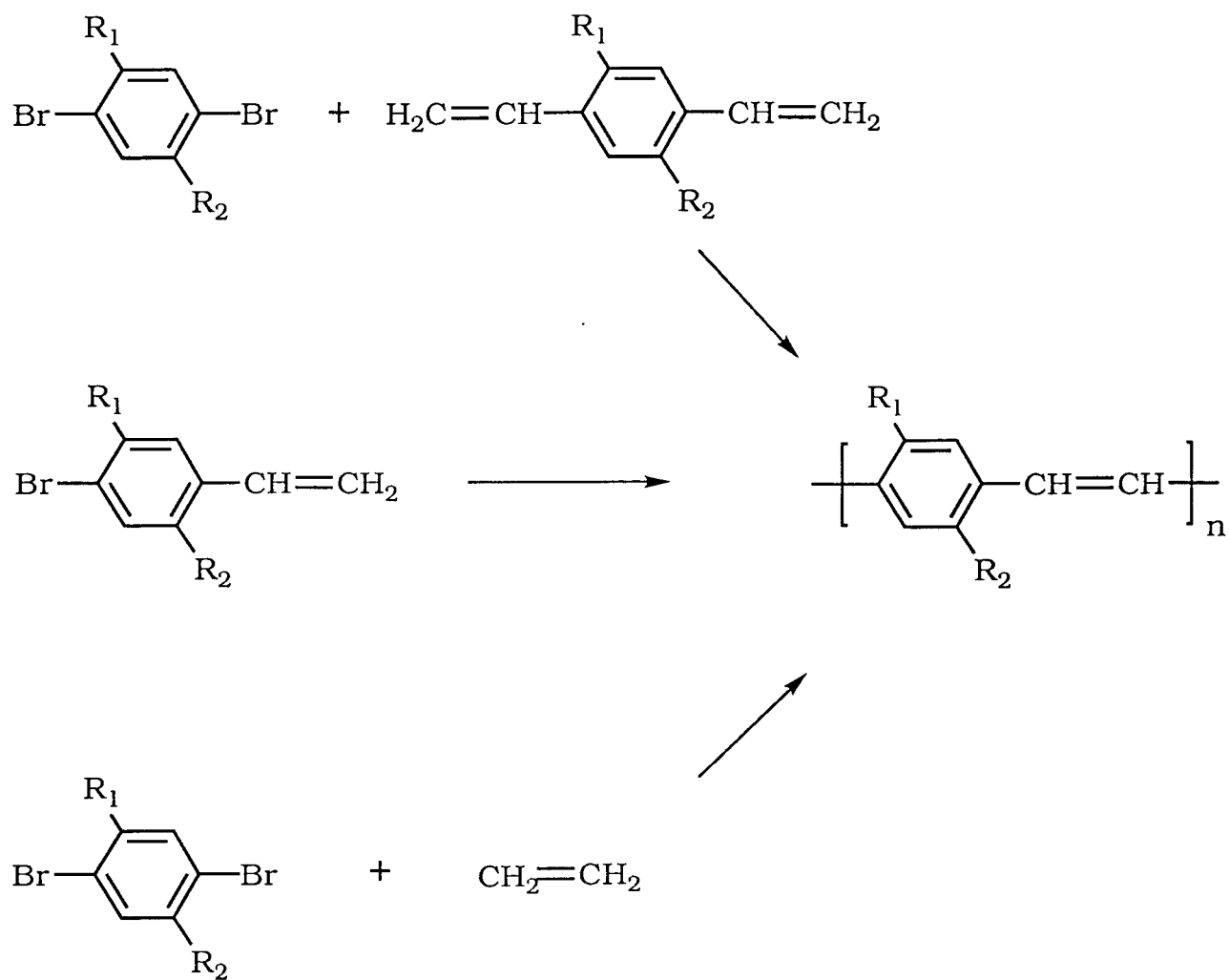




Scheme 15

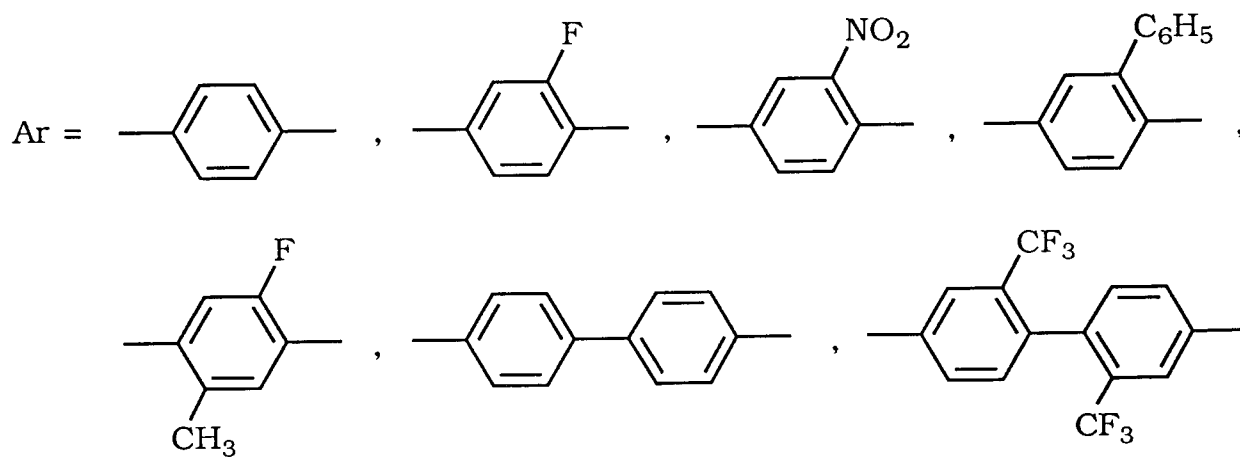
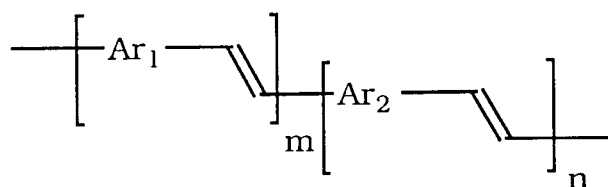
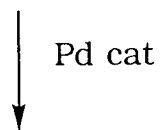
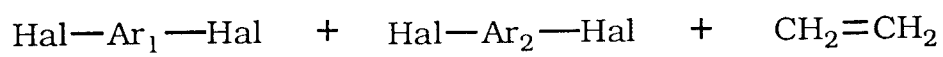


Scheme 16

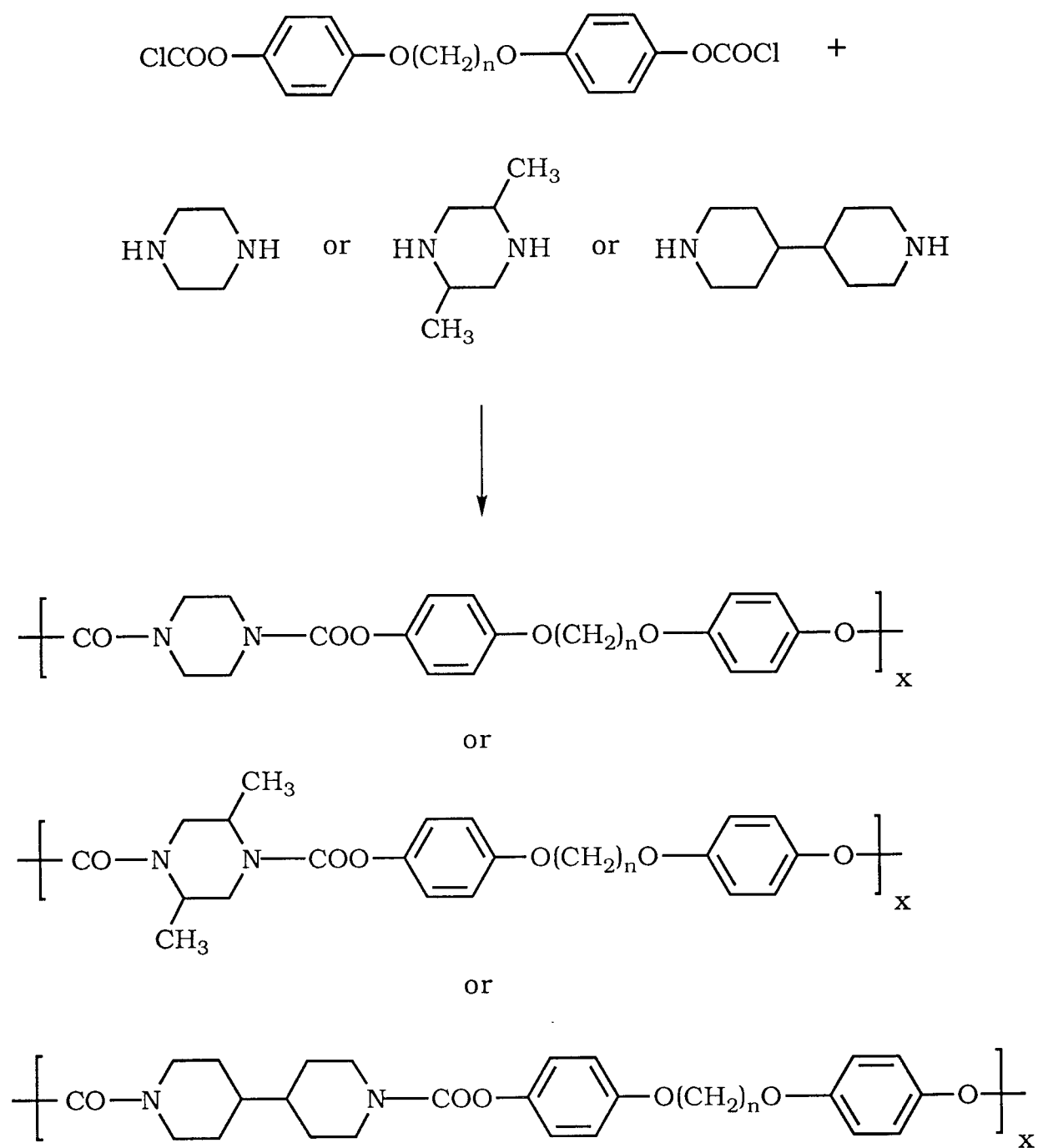


$\text{R}_1 = \text{R}_2 = \text{H}$; $\text{R}_1 = \text{H}, \text{R}_2 = \text{CH}_3, \text{CF}_3 \text{ or } \text{C}_6\text{H}_5$; $\text{R}_1 = \text{R}_2 = \text{CH}_3$

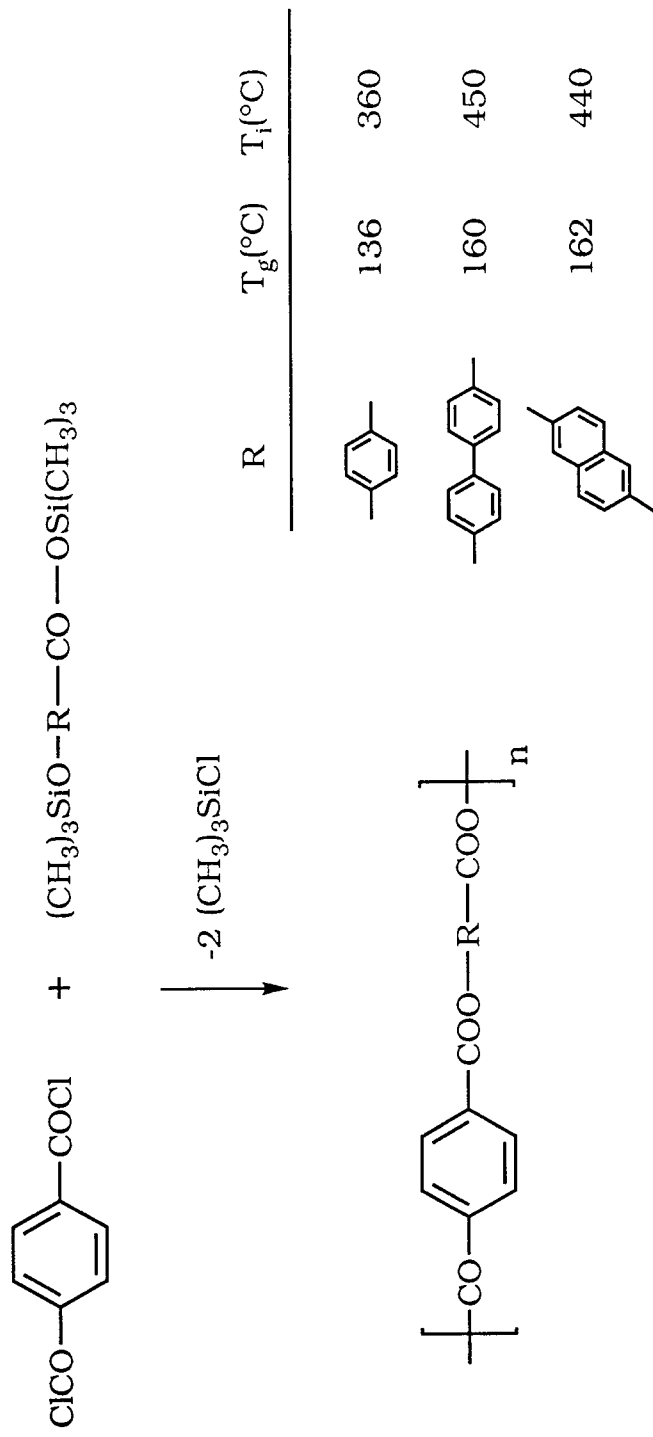
Scheme 17



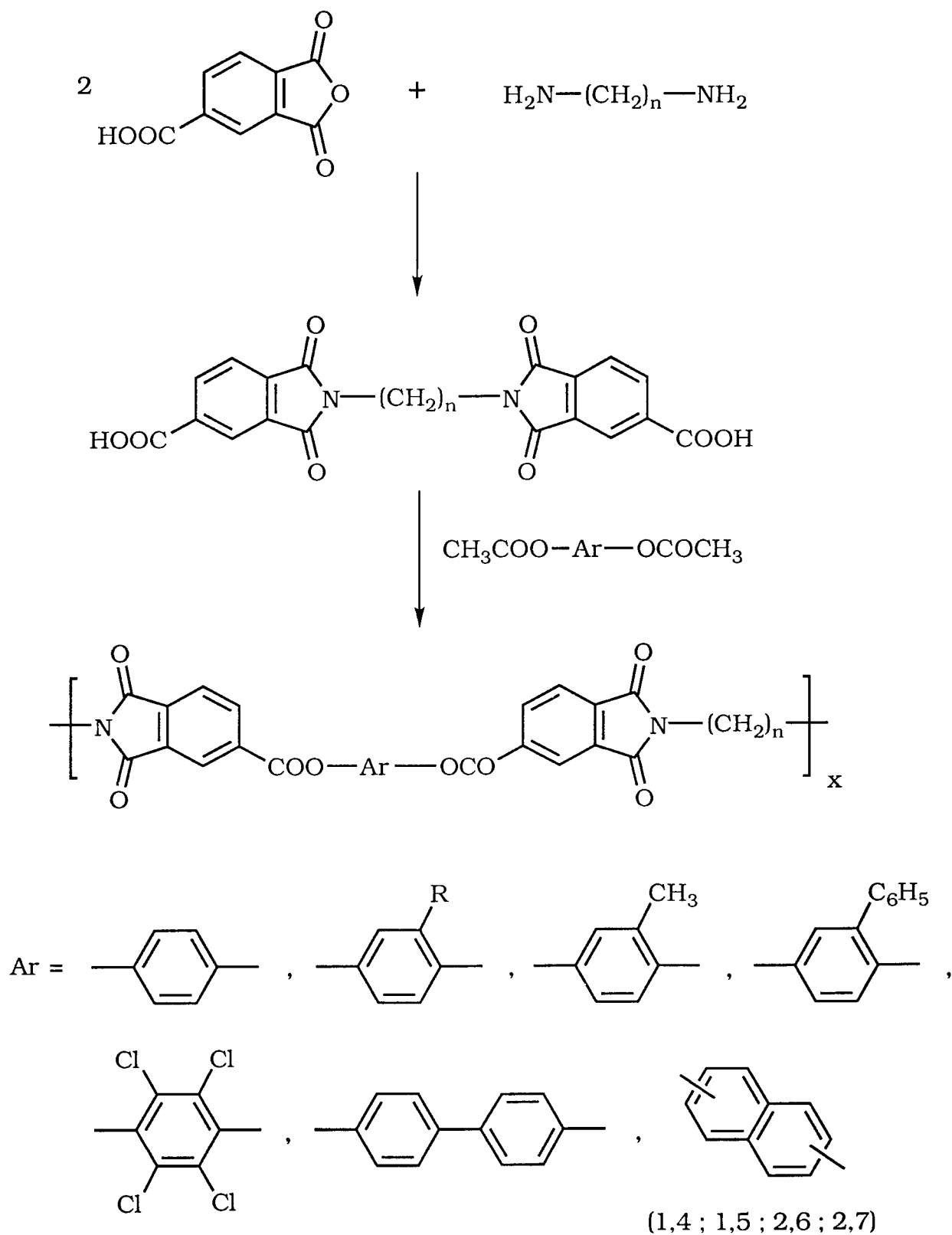
Scheme 18



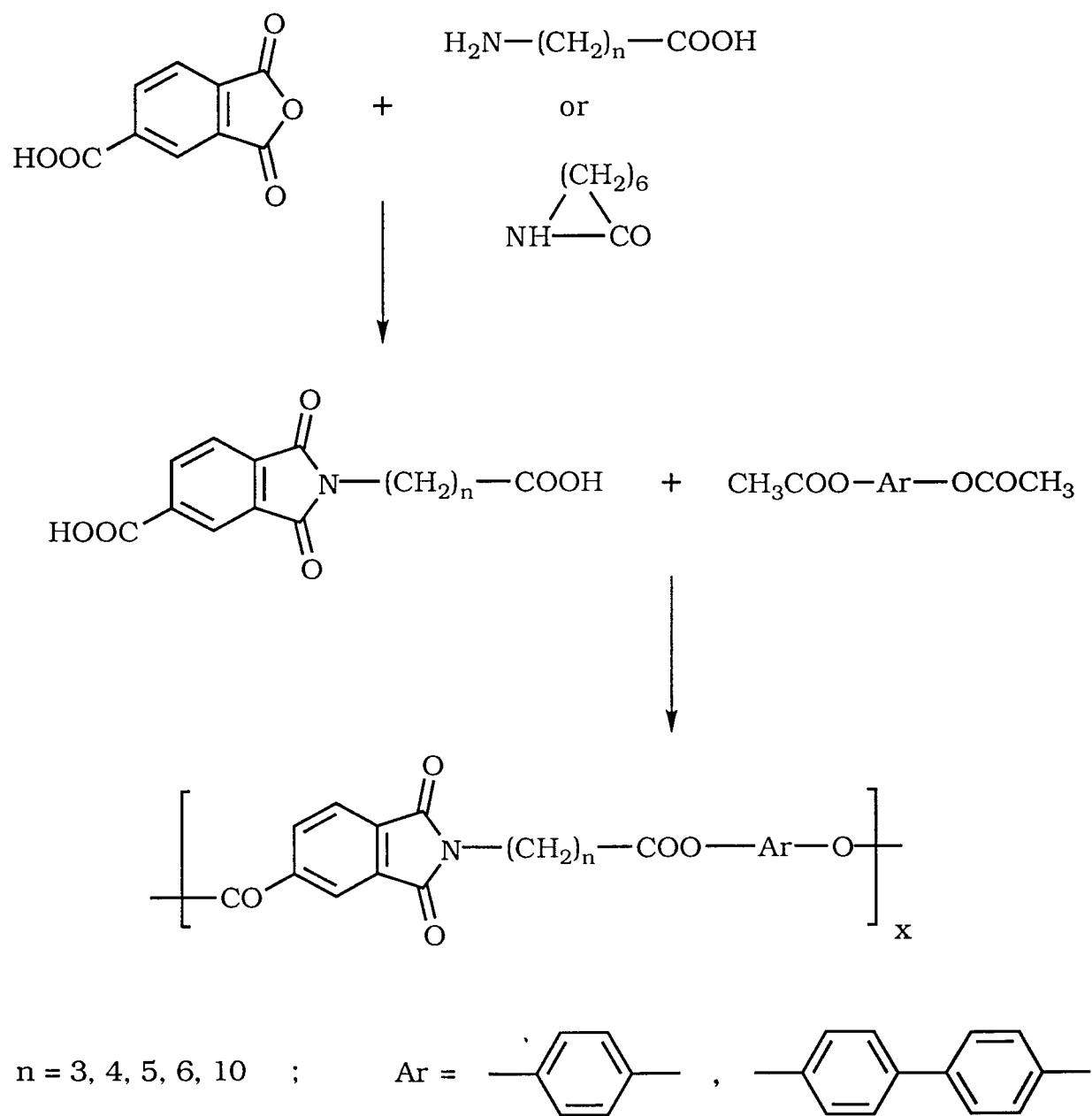
Scheme 19



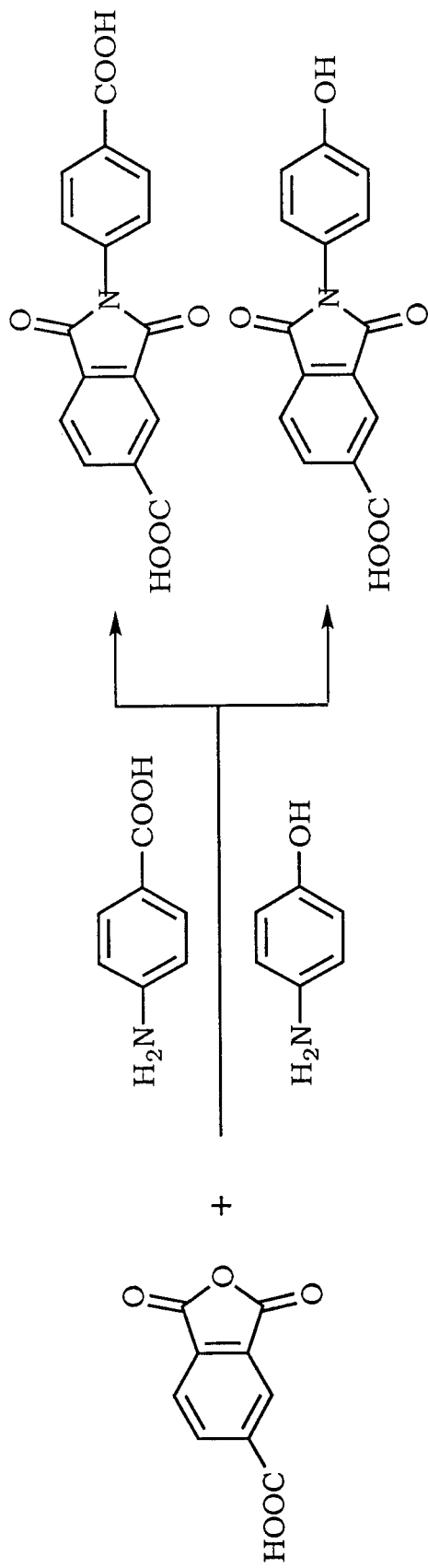
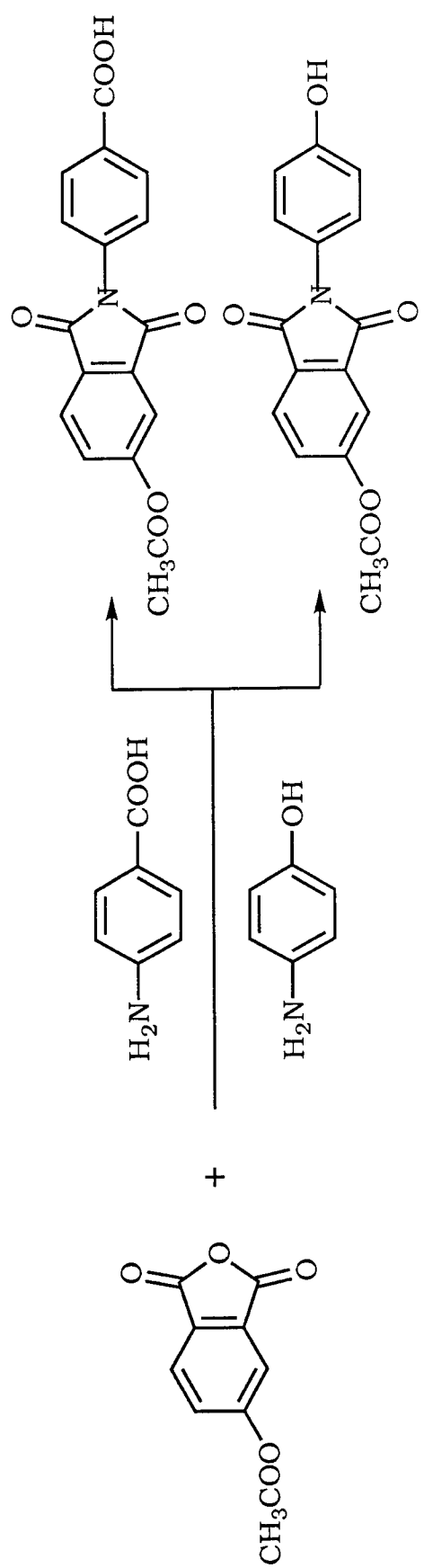
Scheme 20



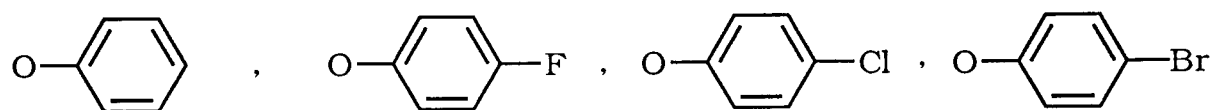
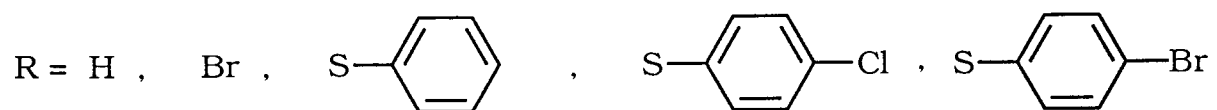
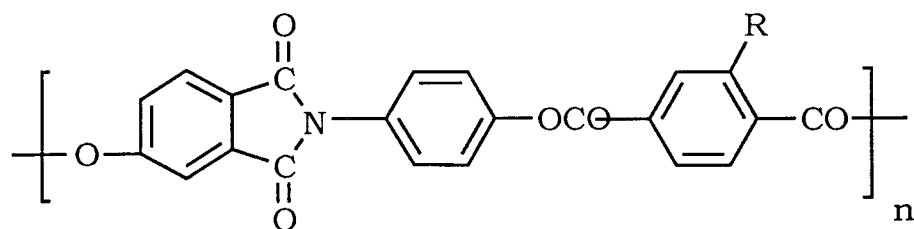
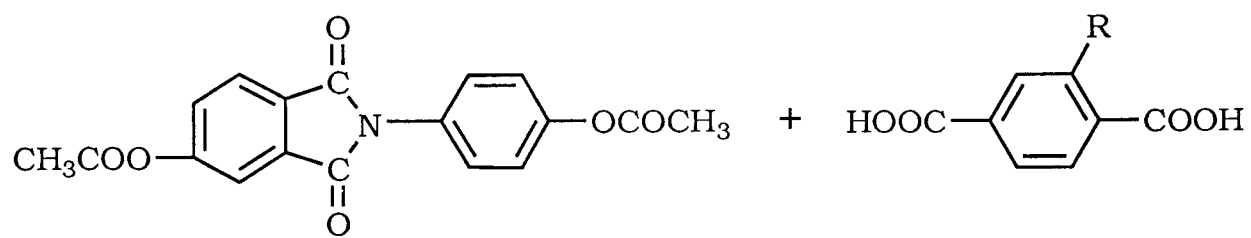
Scheme 21



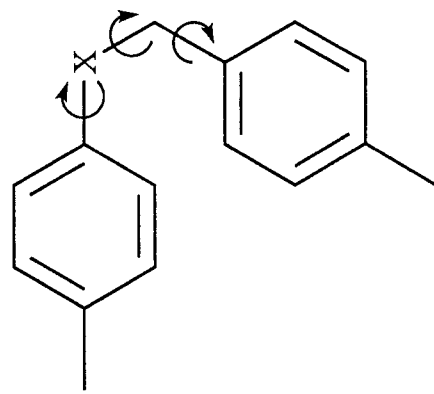
Scheme 22



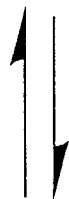
Scheme 23



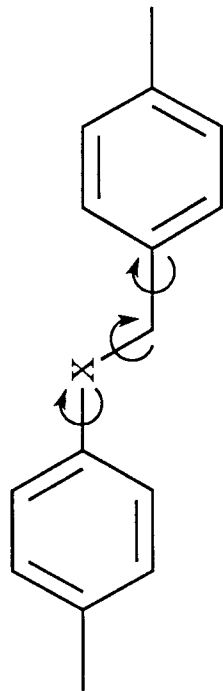
Scheme 24



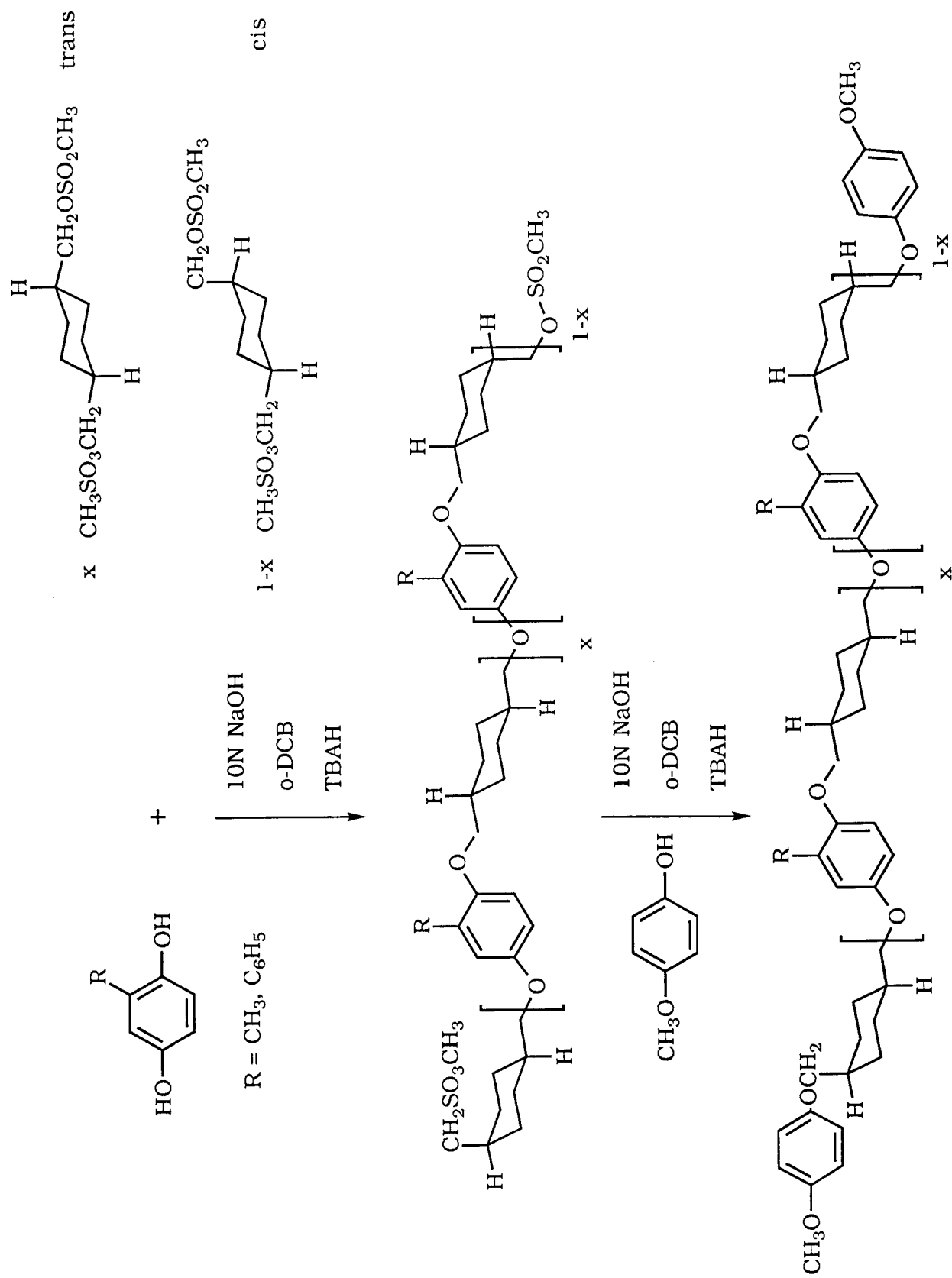
GAUCHE



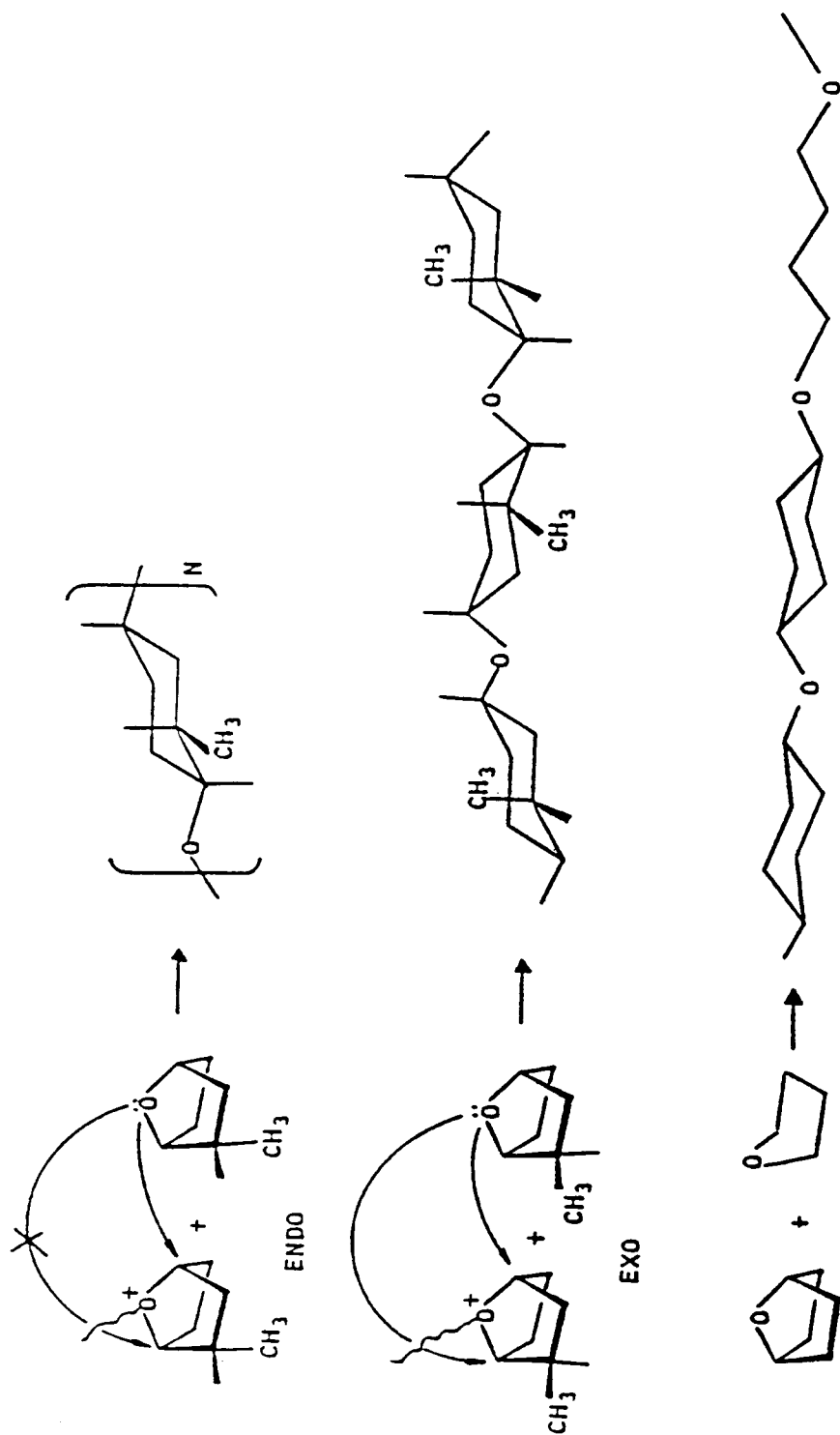
$X = -CH_2^-, O$



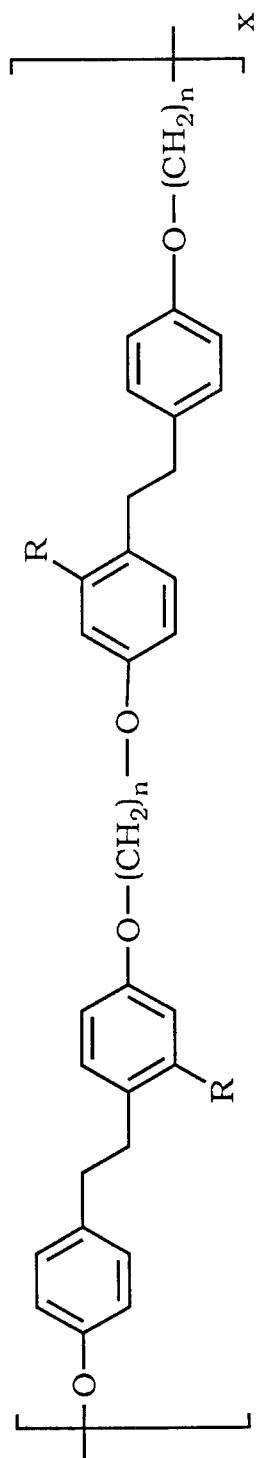
ANTI



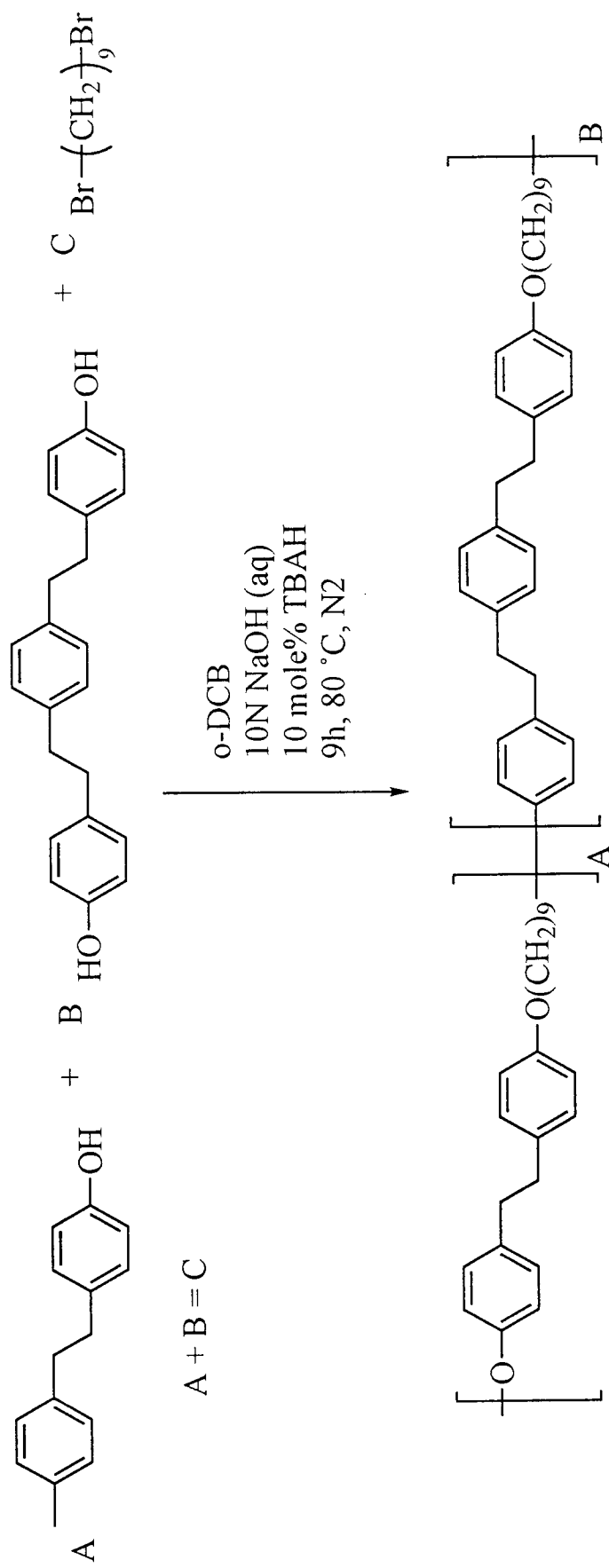
Scheme 26



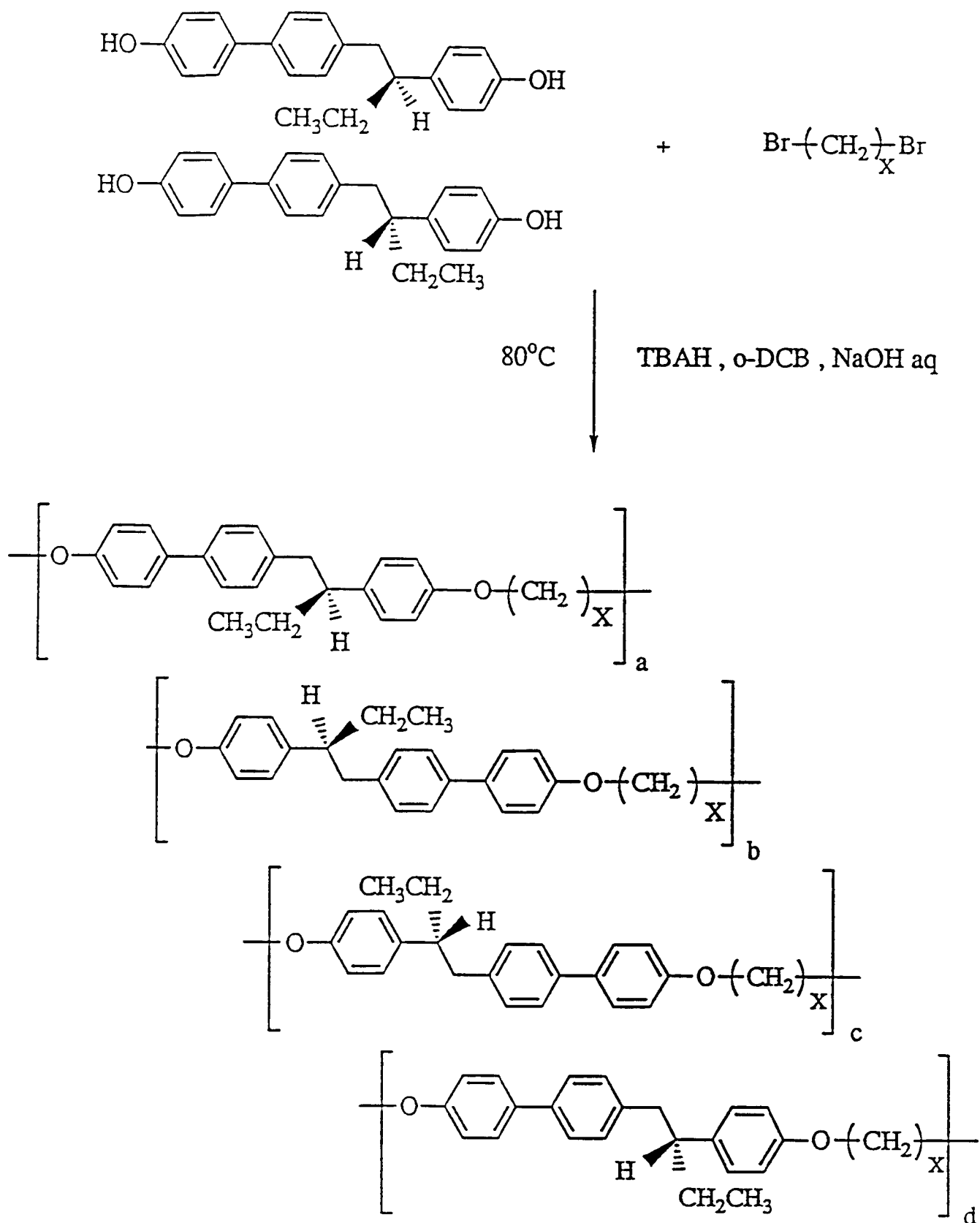
Scheme 27



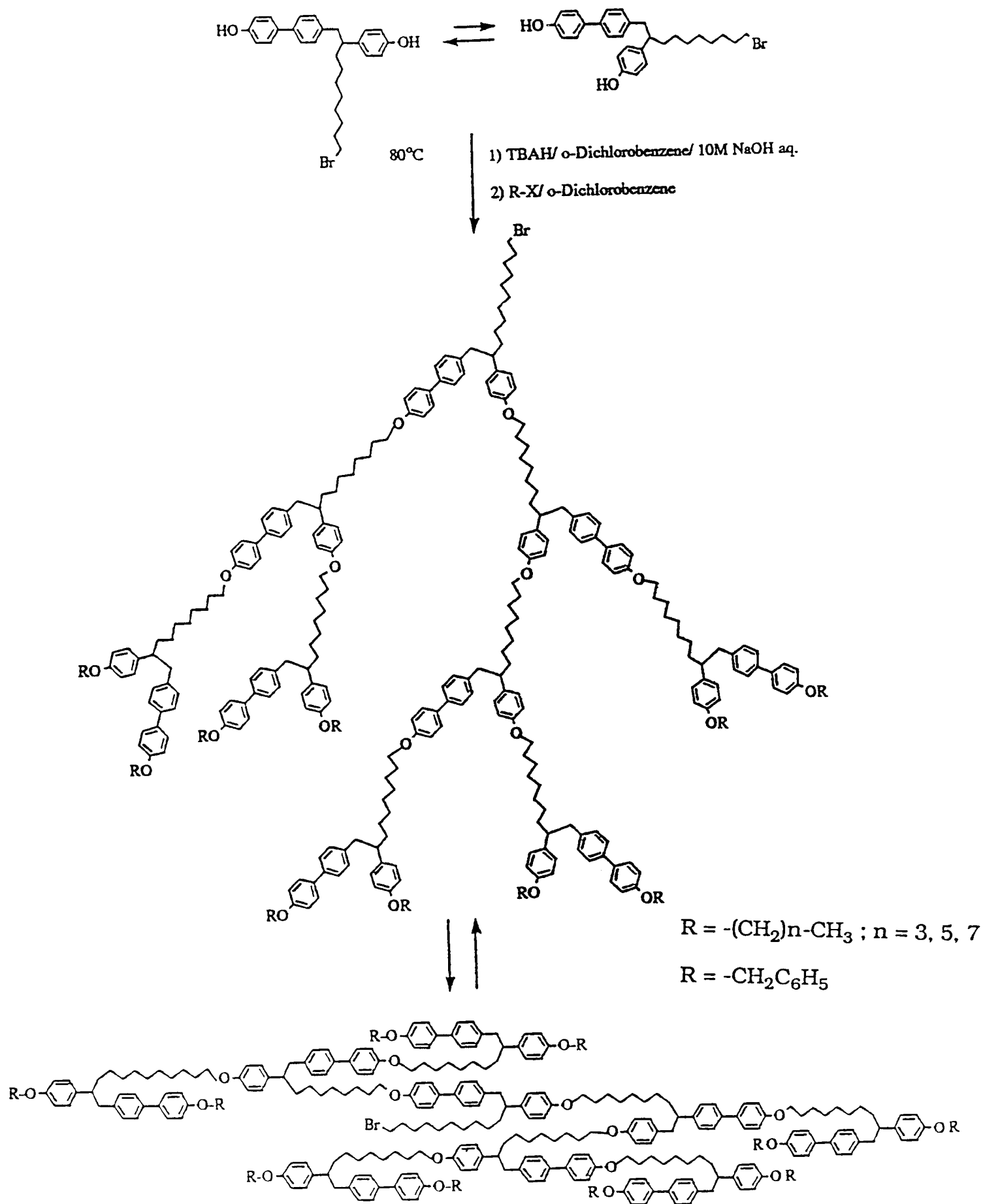
Scheme 28



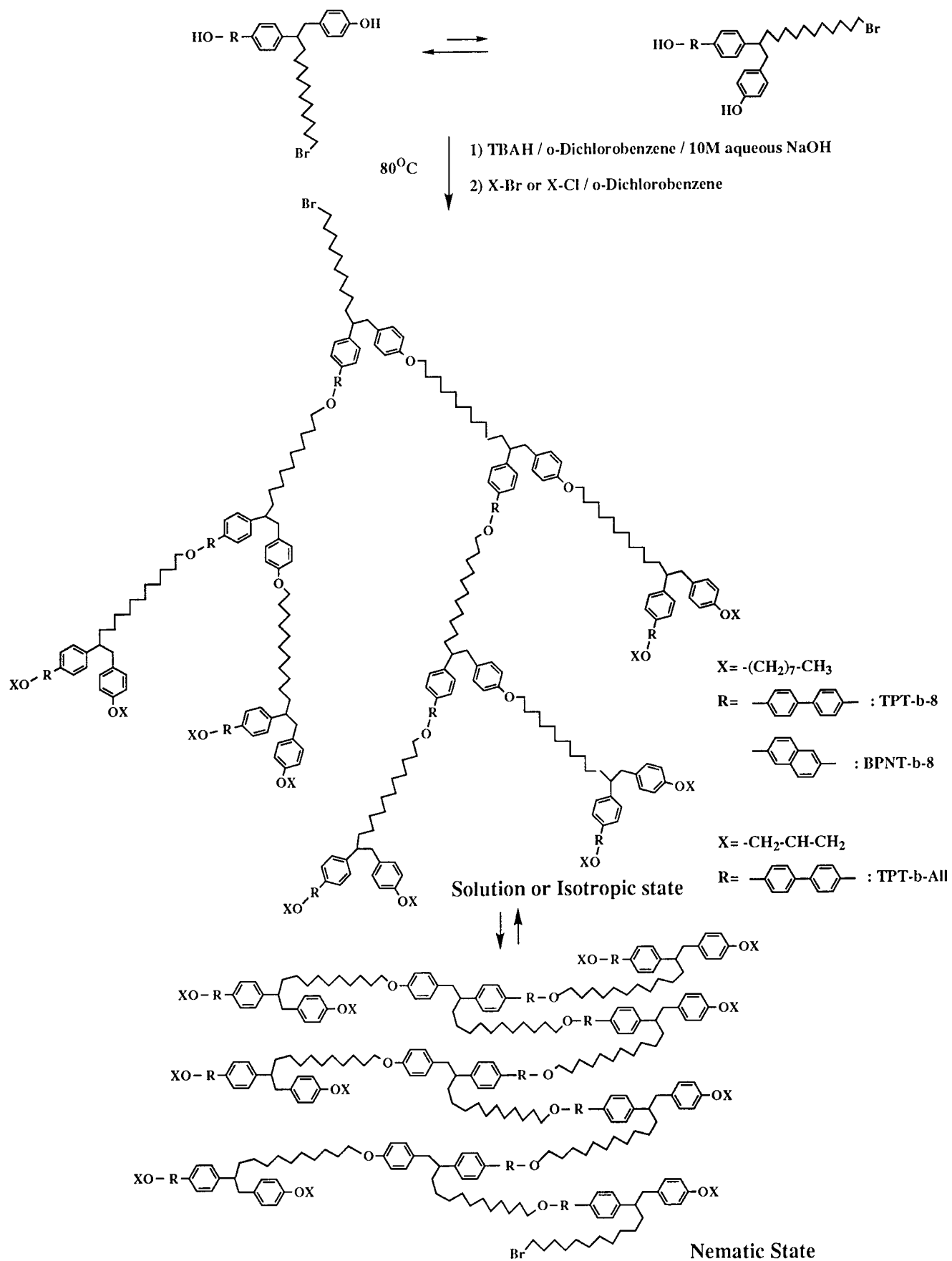
Scheme 29



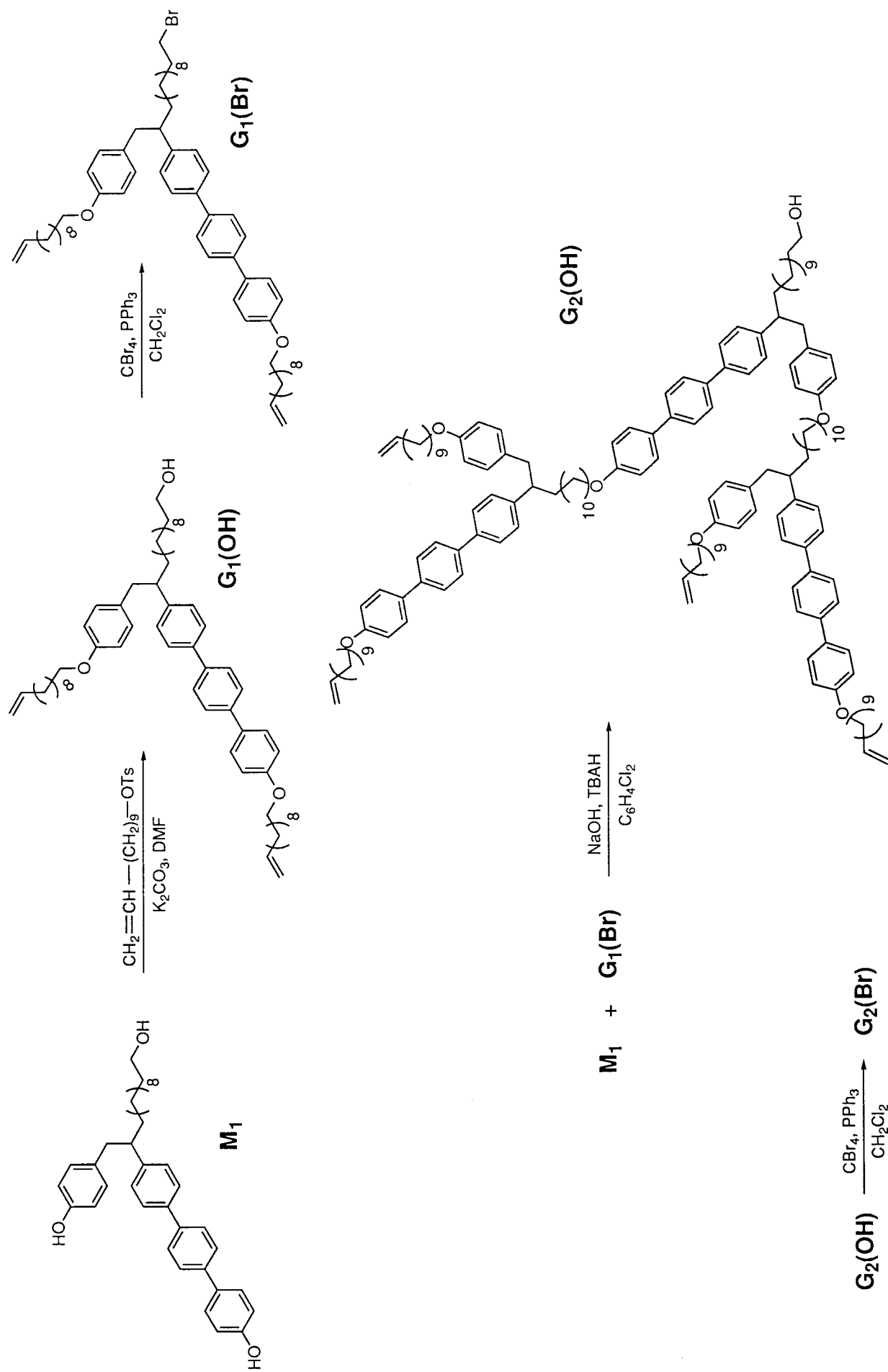
Scheme 30



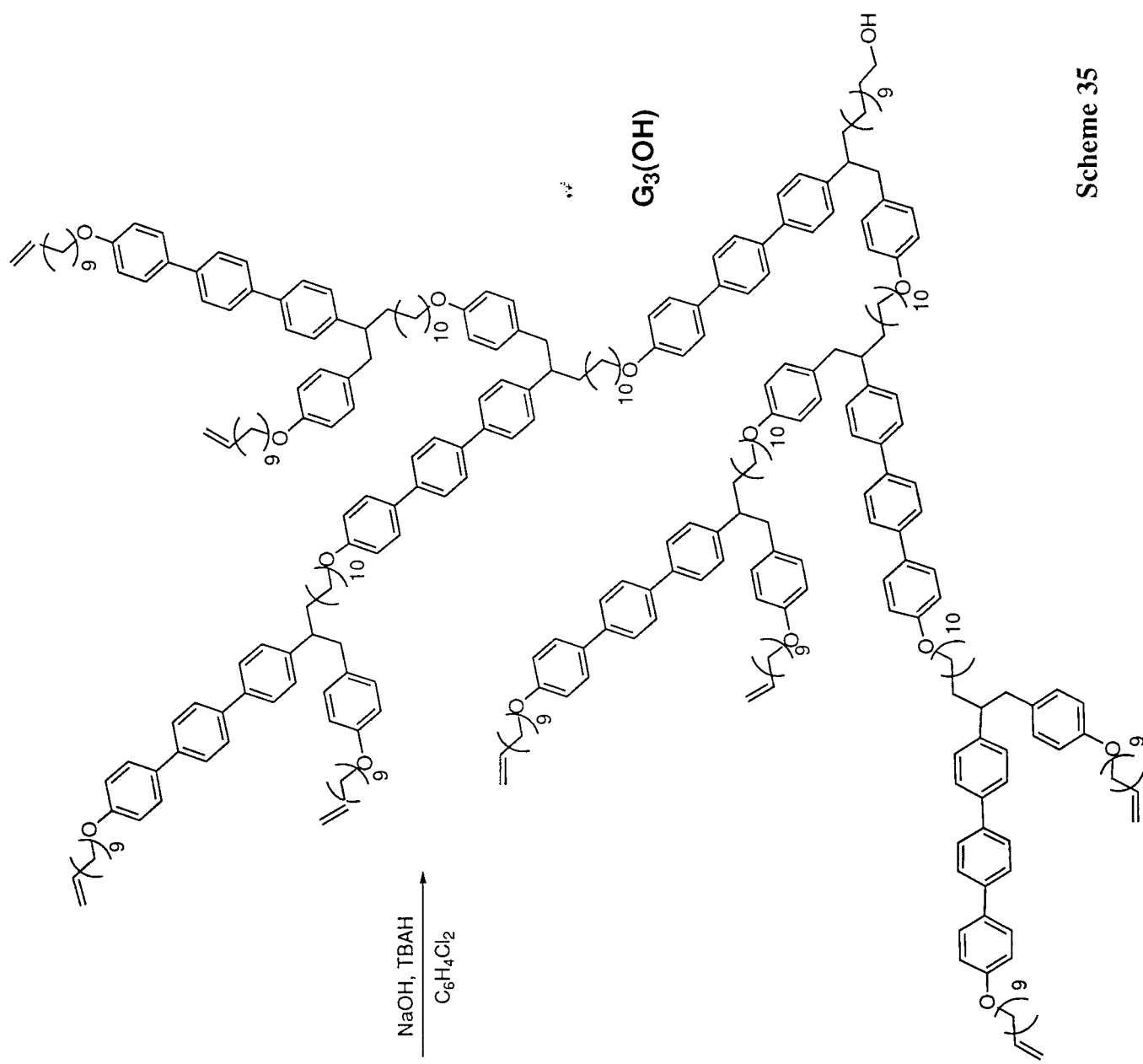
Scheme 32



Scheme 33

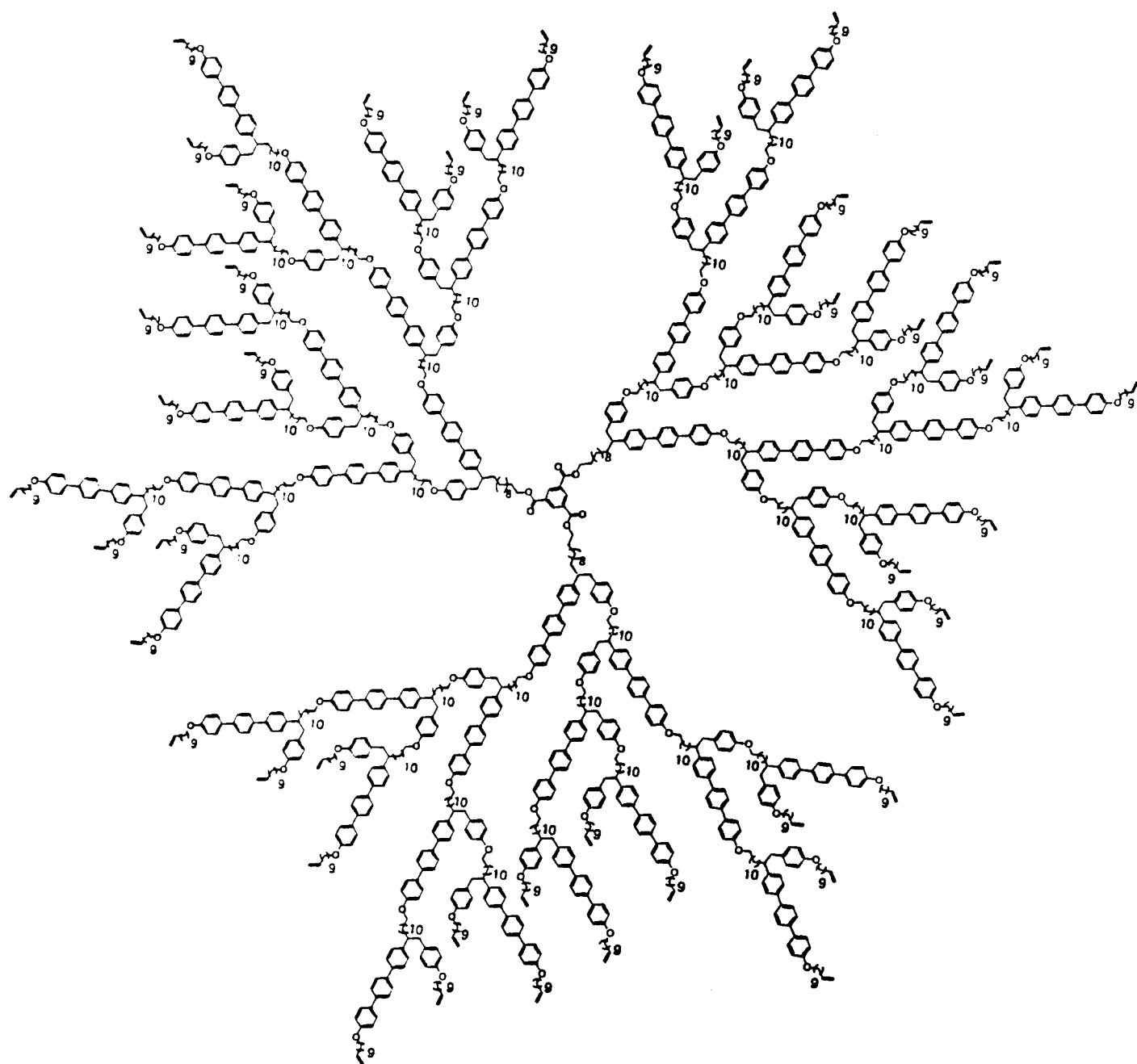


Scheme 34

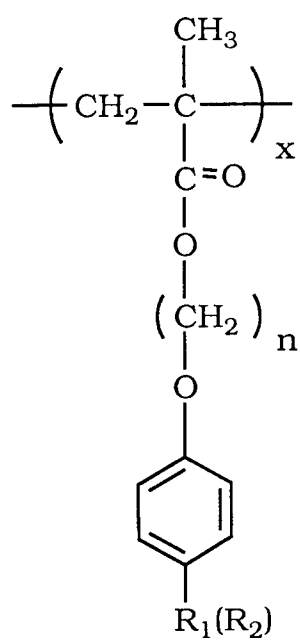


Scheme 35

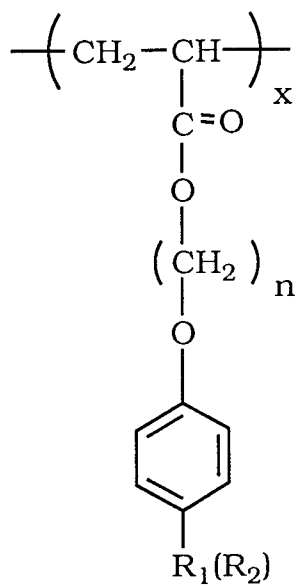




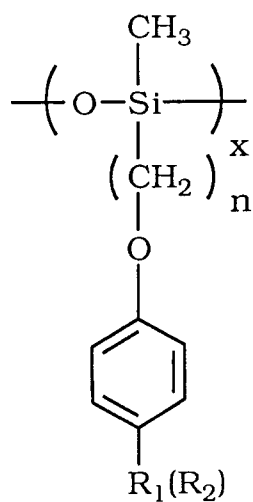
Scheme 37



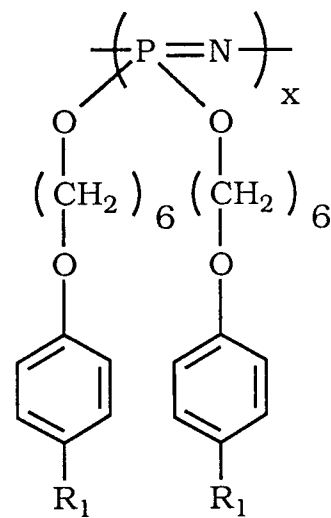
4(4')-n-PMA



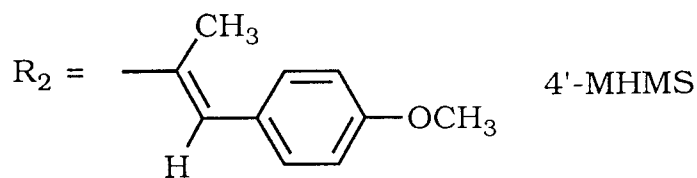
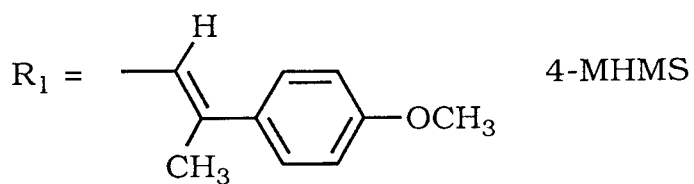
4(4')-n-PAC



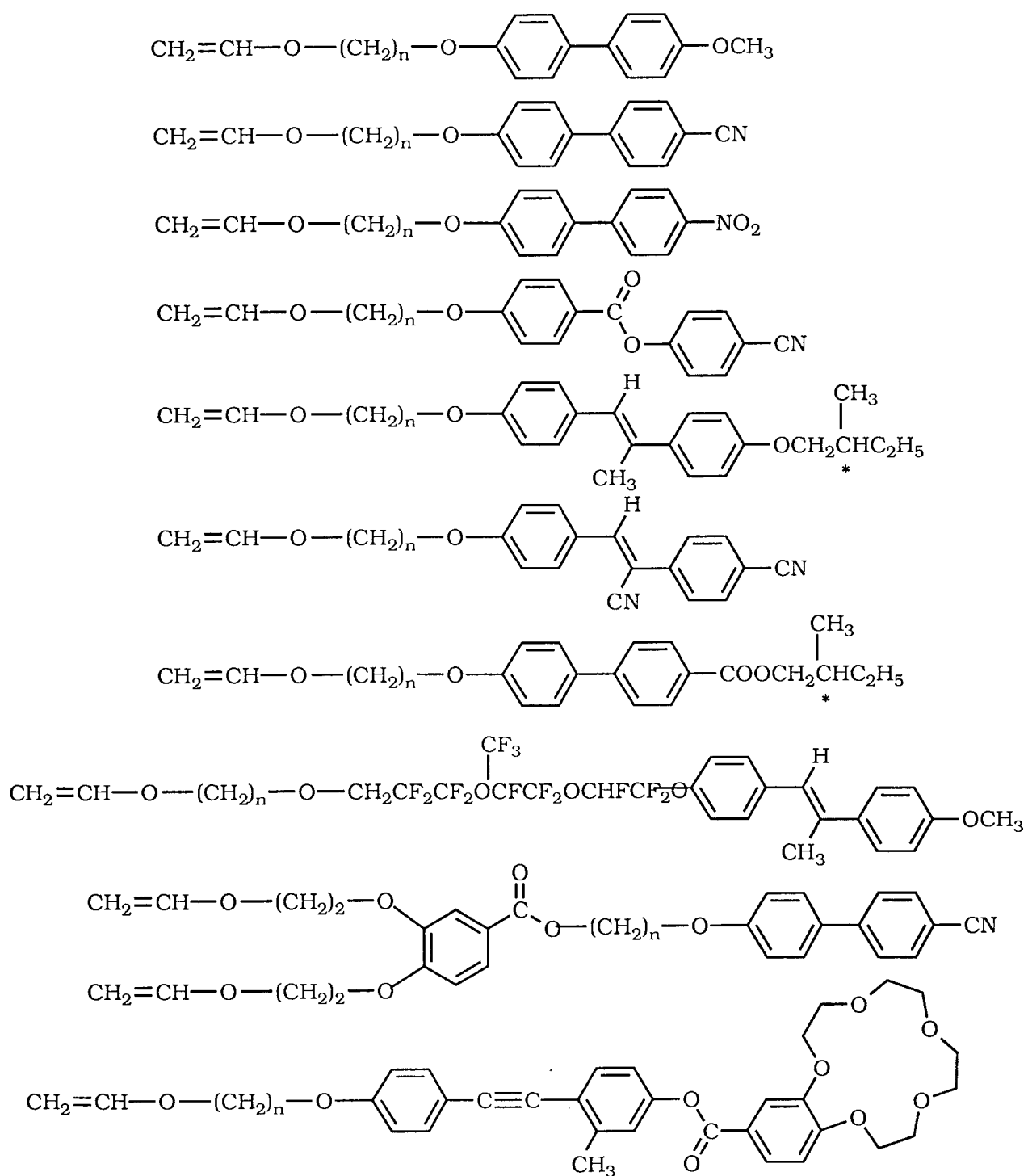
4(4')-n-PS



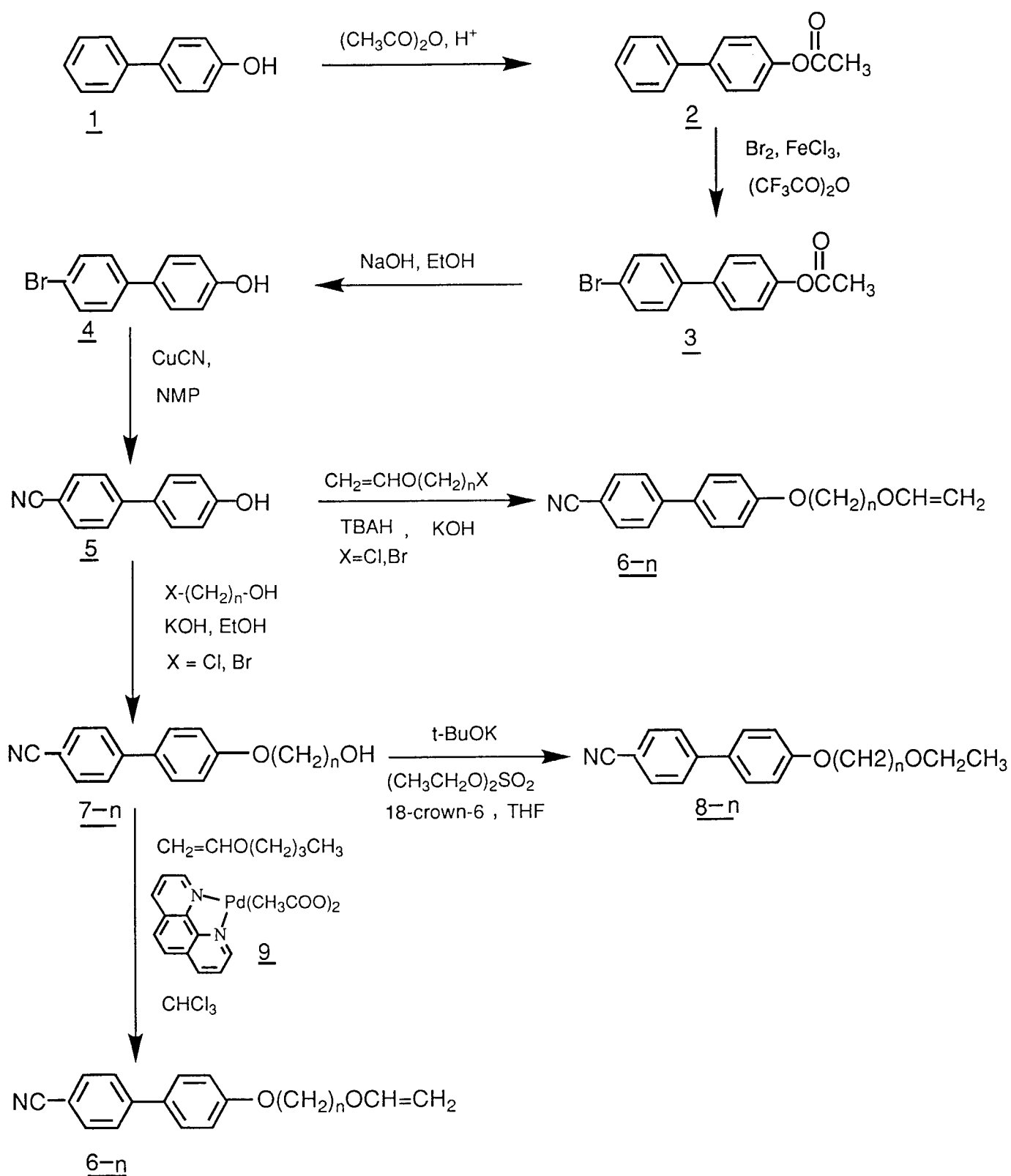
4-6-PPA



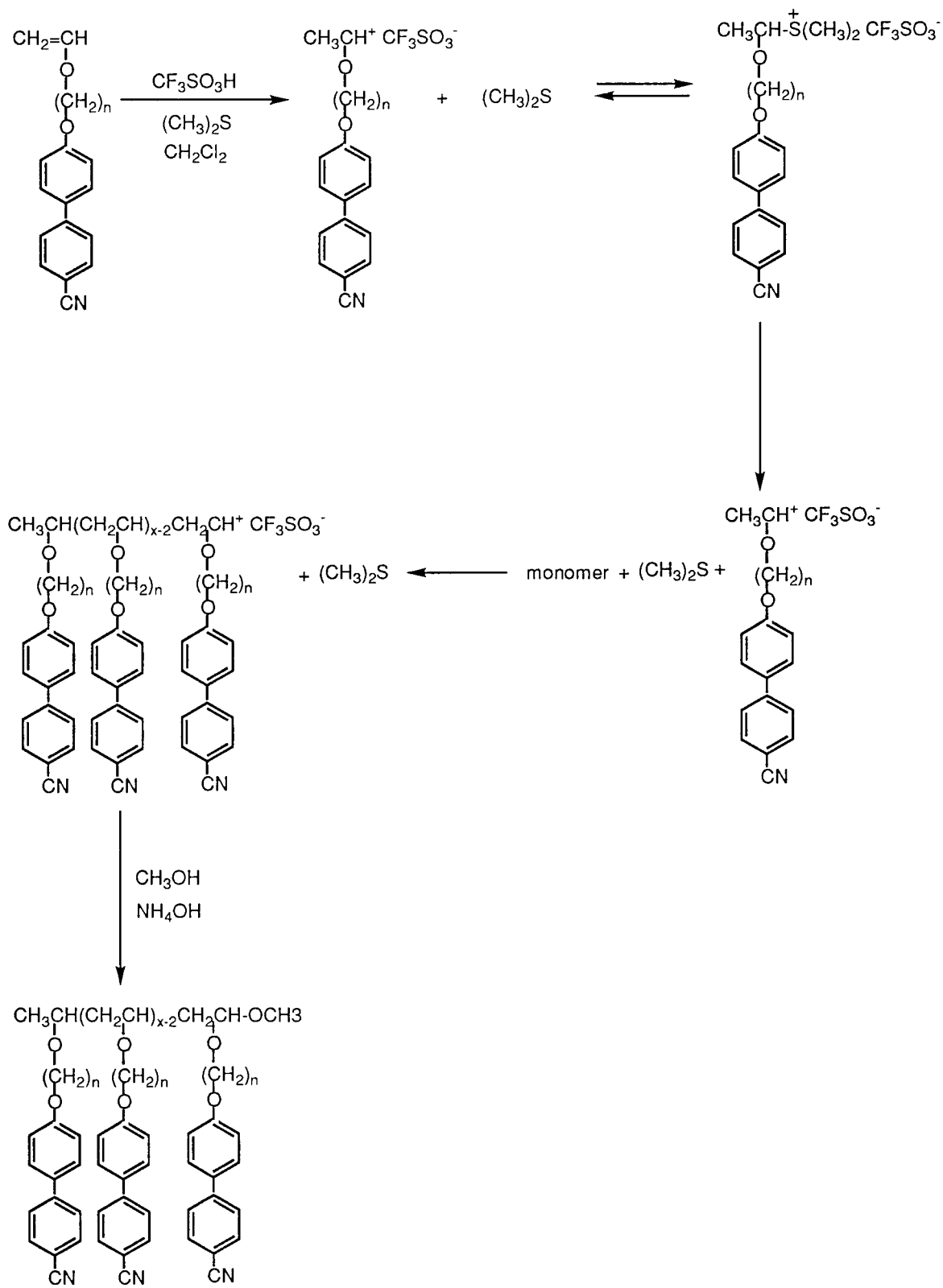
$n = 3, 6, 8, 11$



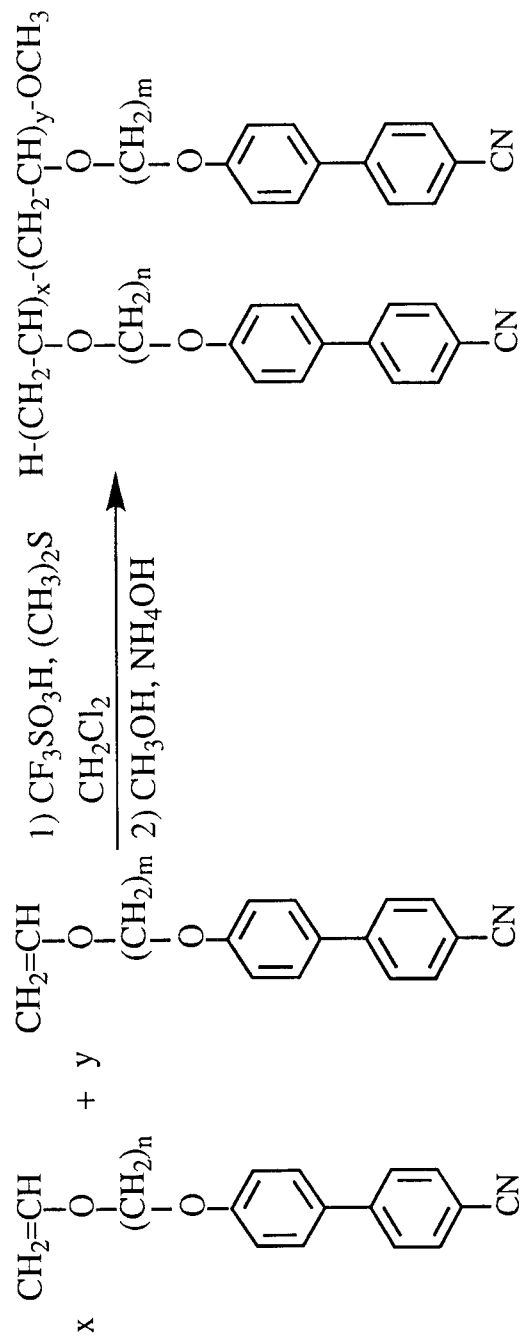
Scheme 39



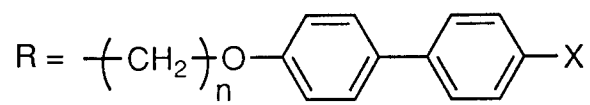
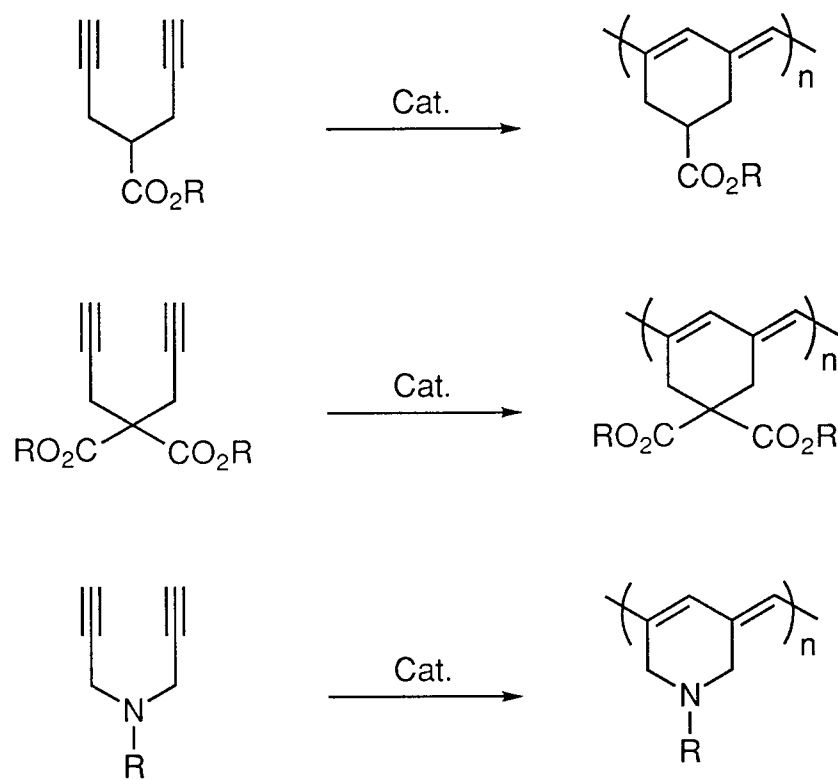
Scheme 40



Scheme 41

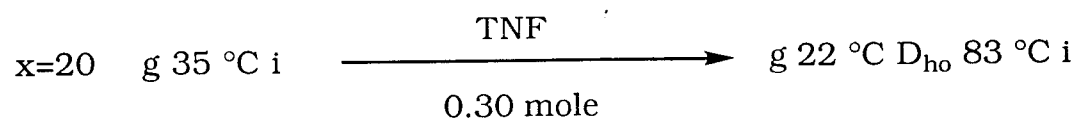
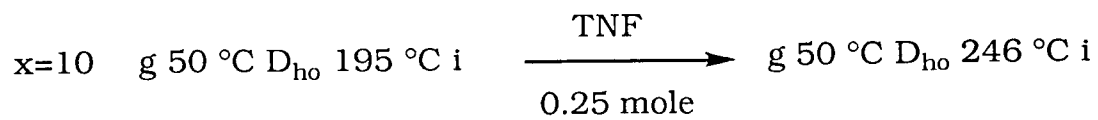
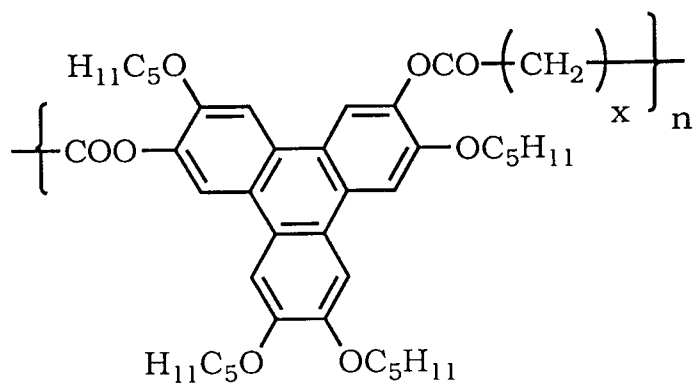


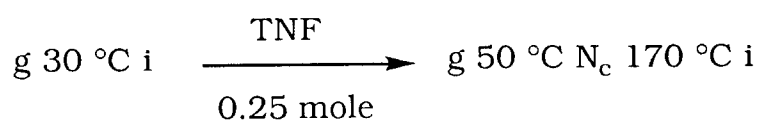
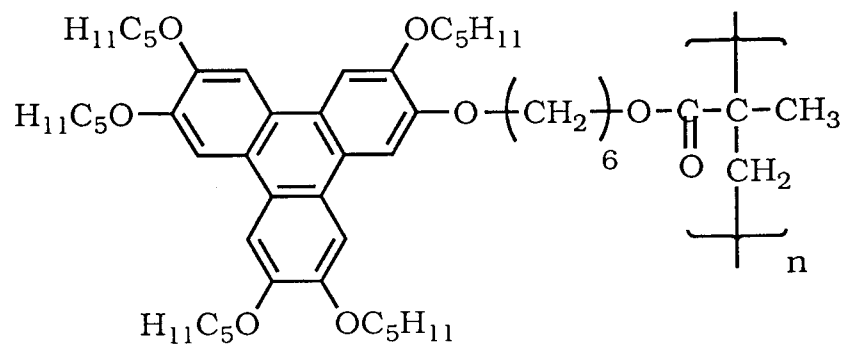
Scheme 42



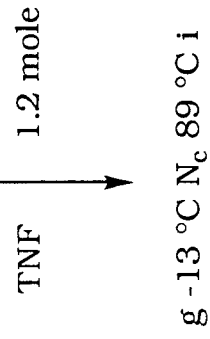
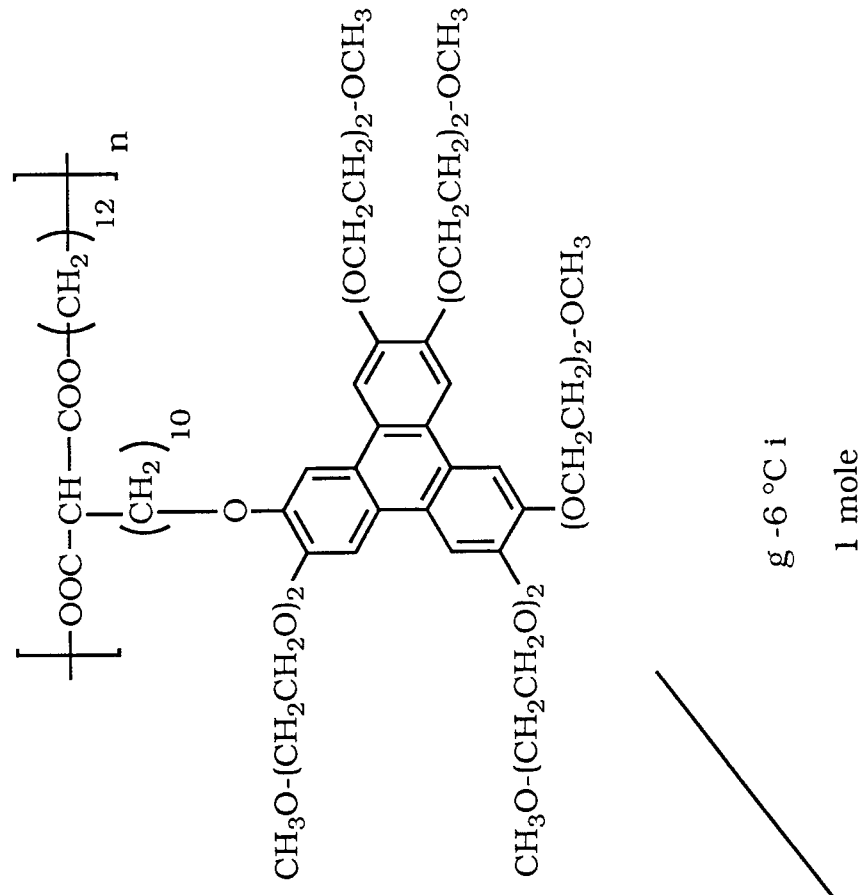
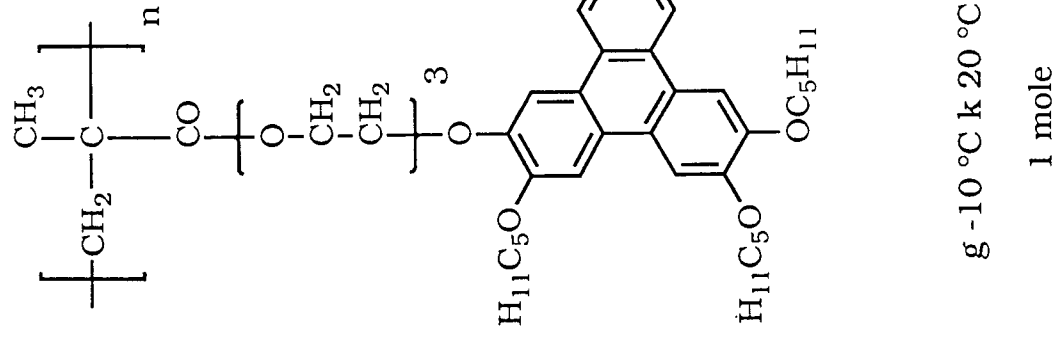
$\text{X} = \text{OCH}_3, \text{CN}$

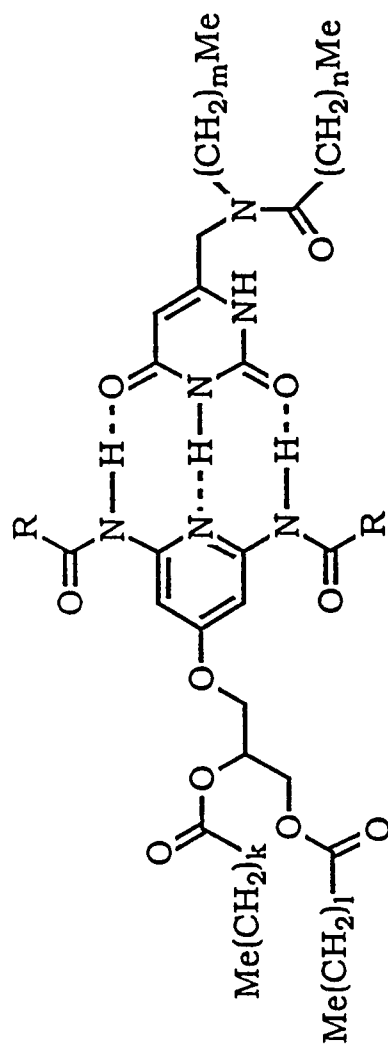
Scheme 43



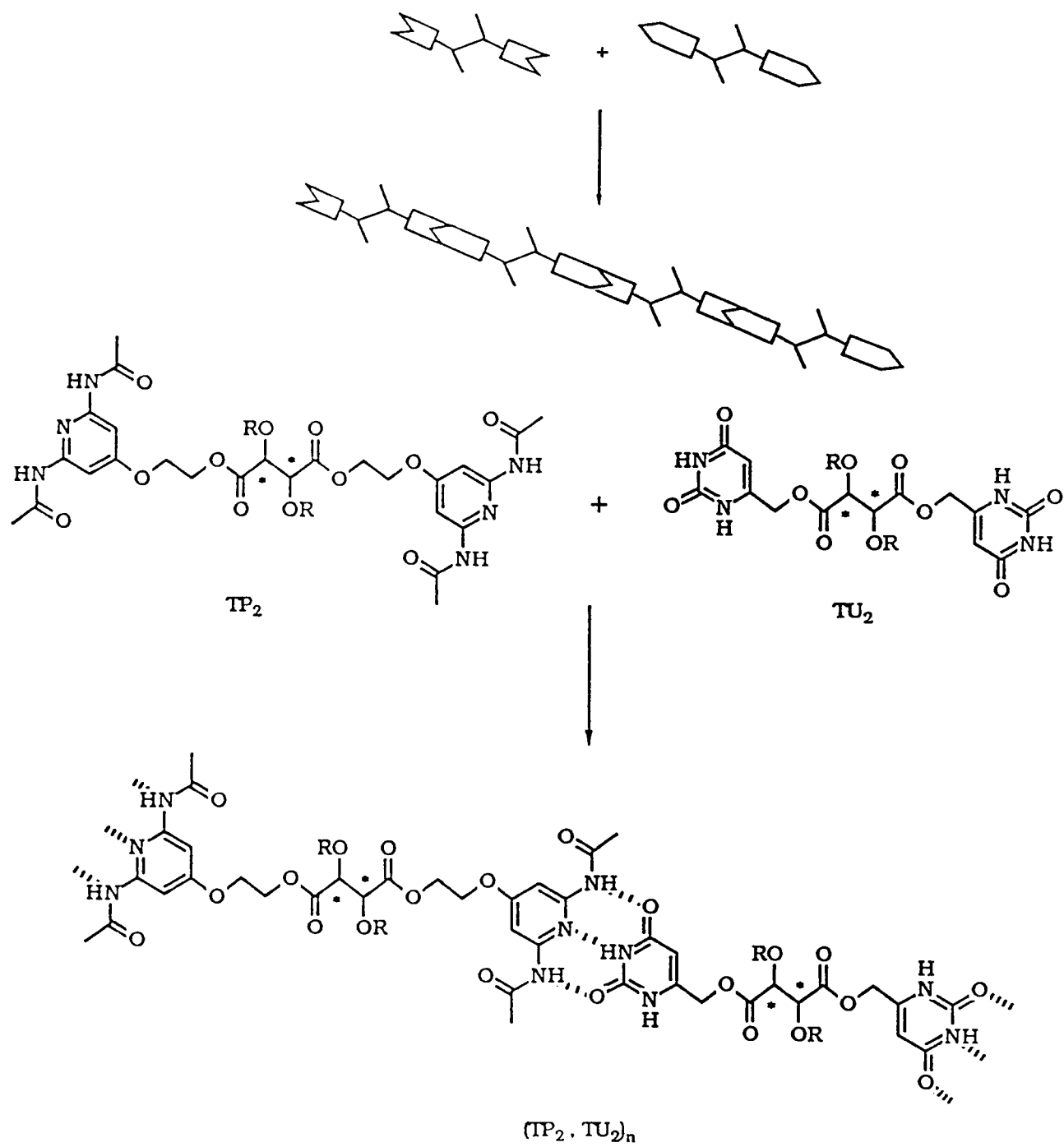


Scheme 45





Scheme 47



Scheme 48

